Universidade de Aveiro Departamento de Química
Ano 2010

João Miguel Nunes Silva

Synthesis of polyesters derived from 2,5-furandicarboxylic acid

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Materiais Derivados de Recursos Renováveis, realizada sob a orientação científica do Prof. Doutor Armando Silvestre e do Prof. Doutor Alessandro Gandini do Departamento de Química da Universidade de Aveiro.

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Palavras-passe

Recursos renováveis, biomassa, hidratos de carbono, 5-hidroximetilfurfural, ácido 2,5-furanodicarboxílico, policondensação em estado fundido, policondensação interfacial, poliésteres.

resumo

O interesse em materiais poliméricos a partir de recursos renováveis tem crescido fortemente nos últimos anos como reflexo da percepção da escassez futura dos recursos fósseis e riscos ambientais relacionados com a sua exploração. Entre a vasta gama de polímeros de base biológica, a família dos poliésteres furânicos, e particularmente os derivados do ácido 2,5-furanodicarboxílico, constitui uma das mais interessantes, já que alguns destes podem, num futuro próximo, vir a ser potenciais alternativas dos poliésteres mais comercializados em todo o mundo. Desta forma, o principal objetivo deste trabalho foi sintetizar e caracterizar exaustivamente uma série de poliésteres a partir de dois derivados do ácido 2,5-furanodicarboxílico, nomeadamente, o 2,5-furanodicarboxilato de dimetilo e o dicloreto de 2,5-furanodicarbonilo, e diversos dióis.

Os poliésteres foram sintetizados por métodos convencionais de policondensação, nomeadamente, a policondensação interfacial, combinando o dicloreto de 2,5-furanodicarbonilo com 2,5-bis(hidroximetil)furano, e policondensação em estado fundido, combinando o 2,5-furanodicarboxilato de dimetilo com 1,4-ciclohexanodimetanol e 1,4-butanodiol.

Os materiais obtidos foram caracterizados em detalhe por FTIR, RMN de ^{1}H e ^{13}C, difração de raios-X, análise elementar, e as suas características térmicas foram medidas por DSC e TGA.

Poliésters lineares, possuindo uma estrutura regular, peso molecular razoavelmente elevados e alto grau de cristalinidade, foram preparados. Excepto o poliéster totalmente furânico, todos os poliésteres são termicamente estáveis até 300 º C. As suas características térmicas variam significativamente com a natureza do diol.

Curiosamente, o poli(butileno 2,5-furanodicarboxilato), PBF, apresenta propriedades térmicas semelhantes às dos seus homólogos furânicos, PFE e PPF, com Tg de ~ 15, Tc de ~ 65, e Tm de aproximadamente 135 º C.

keywords

Renewable resources, biomass, carbohydrates, 5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, melt polycondensation, interfacial polycondensation, polyesters.

abstract

Interest in polymeric materials from renewable resources has strongly grown in the last few years as reflection of the perceived future scarcity of fossil resources and environmental risks related with their exploitation. Among the wide range of biobased polymers, the realm of furan polyesters, and particularly those derived from 2,5-furandicarboxylic acid, constitutes one of the most interesting classes, since some of them may, in the near future, become competitive replacements of the most commercialized polymers worldwide. So, it was the main purpose of this work to synthesize and thoroughly characterize a series of polyesters from two 2,5-furandicarboxylic acid derivatives, namely its dimethyl ester and dichloride, and diverse diols.

Polyesters were synthesized by conventional polycondensation methods, namely interfacial polycondensation, by combining the diacid dichloride with 2,5-bis(hydroxymethyl)furan, and melt polycondensation, by combining the diacid dimethyl ester with 1,4-cyclohexanedimethanol and 1,4-butanediol.

The ensuing materials were thoroughly characterized by FTIR, 1H and 13C NMR, X-ray diffraction, elemental analysis, and their thermal features were measured by DSC and TGA.

Polyesters, possessing a regular structure, reasonably high molecular weights, and high degree of crystallinity, were prepared.

Except the fully furanic polyester, all of the polyesters were found to be thermally stable up to 300 ºC. Their thermal features were found to vary significantly with the nature of the diol.

Interestingly, Poly(butylene 2,5-furandicarboxylate), PBF, presents similar thermal properties as those reported for its furan homologues PEF and PPF, with Tg of ~15, Tc of ~65, and Tm of ~135 ºC.

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Background

Throughout human history, biobased products represented the basis to meet society needs in terms of energy, chemicals, and materials until nearly the end of the 19th century. Since then, with the advent of coal, natural gas, and petroleum chemistry, chemical industry has been producing a wide range of chemicals (together with energy and fuels) from fossil resources (first from coal and later from petroleum and natural gas) which represent the basis for the synthesis of most of the products, including polymers and other organic chemicals used in modern society daily life. As a result, the contribution of biobased products was reduced to very modest levels (Fig. 1).[1-3]

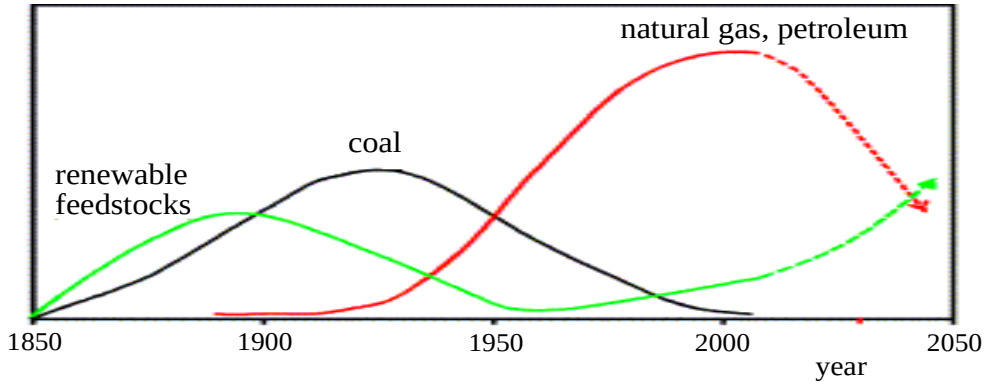


Fig. 1. Raw materials basis of chemical industry throughout history.[3]

Nearing the end of the last century, the awareness on the three aspects, viz.: (i) the progressive depletion and perceived future scarcity of the fossil reserves (according to expert predictions the future availability of either petroleum or natural gas ranges from one to three generations);[4,5] (ii) the environmental risks associated with their excessive consumption; and (iii) the unstable prices of petroleum (experts predict the end of cheap oil by 2040 at latest),[6,7] raised serious questions regarding their exploitation in the long-term. Since then, the exploitation of biomass for the production of power/energy, fuels, chemicals and materials, has been seen as one of the major key issues to achieve a sustainable development.

This renewed interest in producing biobased products has directed the scientific and commercial interest towards the development of new industries, known as biorefineries, incorporating refining strategies to convert biomass into energy, biofuels, platform molecules and finally end products, including polymeric materials.[1,8-12] In this sense, several biorefinery systems have been proposed, including whole-crop, green and

lignocellulosic feedstock (LCF) biorefineries.[8,10,12] Therefore, it is expected that the current industrial processes, largely based on petroleum exploitation, will gradually be replaced by biorefineries, which will produce a number of value-added products capable of replacing those presently obtained from petrochemistry. Obviously, for this shift to be successful, the development of new approaches for converting biomass constituents into biomass-derived compounds is required.

In contrast with fossil fuels, vegetable biomass is renewable, i.e. can be regrown after harvesting; and can be CO_2 neutral.[9,13] Nature produces vegetable biomass in an annual amount of about 180 x 10^9 tons by photosynthesis, of which 75% is assigned to the class of carbohydrates, namely cellulose (a high molecular weight polymer of glucose) and hemicelluloses/polyoses (short-chain polymers of predominantly pentoses), and 20% to lignin, a phenolic polymer.[8,14] These two fractions are therefore the major constituents of vegetable biomass, and together they constitute the so called ‘‘lignocellulosic biomass’’. The remaining part, approximately 5%, consists of natural compounds of different natures, e.g. proteins, fats (oils) and other substances (Fig. 2).[8]

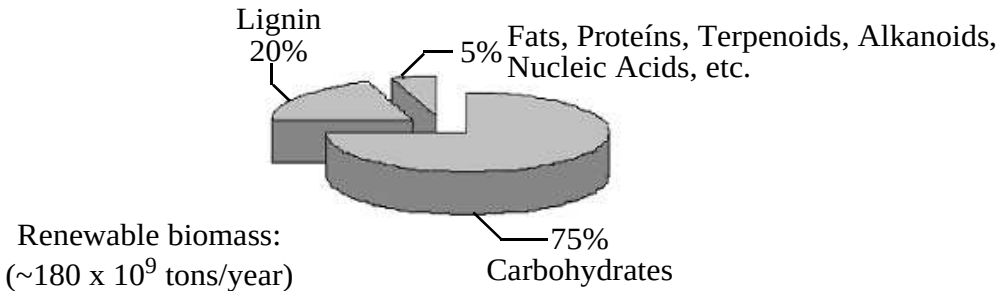


Fig. 2. Distribution of the vegetal biomass constituents in terms of percentage (wt % of dry biomass).[8]

Surprisingly, only 4% of the annually available biomass is used by human kind for food and non-food purposes.[3] Therefore, the main focus for the development of this area should be the efficient access and exploitation of biomass sources and subsequent efficient use of its main components, and particularly carbohydrates, as precursors of a number of basic organic chemicals and corresponding final products, among which polymeric materials.

From the three existing types of biorefineries, the LCF biorefinery is considered the most promising for the large-scale industrial application in the near future. Several reasons explains such prevalence: (i) the raw material situation is optimal (both

agricultural and forest wastes, including bagasse, rice hulls, rice straw, peanut hulls, wheat straw, grass, forest slash, etc., or even paper wastes);[13] (ii) the non-competition with food industry;[11,14] (iii) the possibility of processing of a wide variety of feedstocks in the same plant;[8] (iv) the requirement of a limited number of conversion platforms, mainly the sugar and the thermochemical platforms;[8] (v) the products arising from LCF biorefinery may, in the future, be direct replacements/competitors of existing petrobased chemicals, or novel chemicals/products with new properties for replacement of existing petrobased chemicals or for new and innovative applications.[9,11,12]

Regarding the biorefinery concept, a LCF biorefinery of the 21st century must meet the requirements of a modern, integrated biorefinery, i.e. an approach that optimizes the use of several conversion strategies, such as chemical/biochemical and thermochemical platforms, to provide multiple useful products.[8,10,12] Thus, the most valuable fractions of biomass, e.g. sugars, will be converted by chemical/biochemical transformations to give well-identified platform molecules, and the less valuable fractions, namely biomass wastes and/or fractions not able for being routed through the former conversion platform, will be converted *via* thermochemical processes, mainly gasification and pyrolisys, to give syngas and bio-oil respectively, which may then serve as sources of chemicals/final products and/or fuels/energy (Fig. 3).[11,12,14]

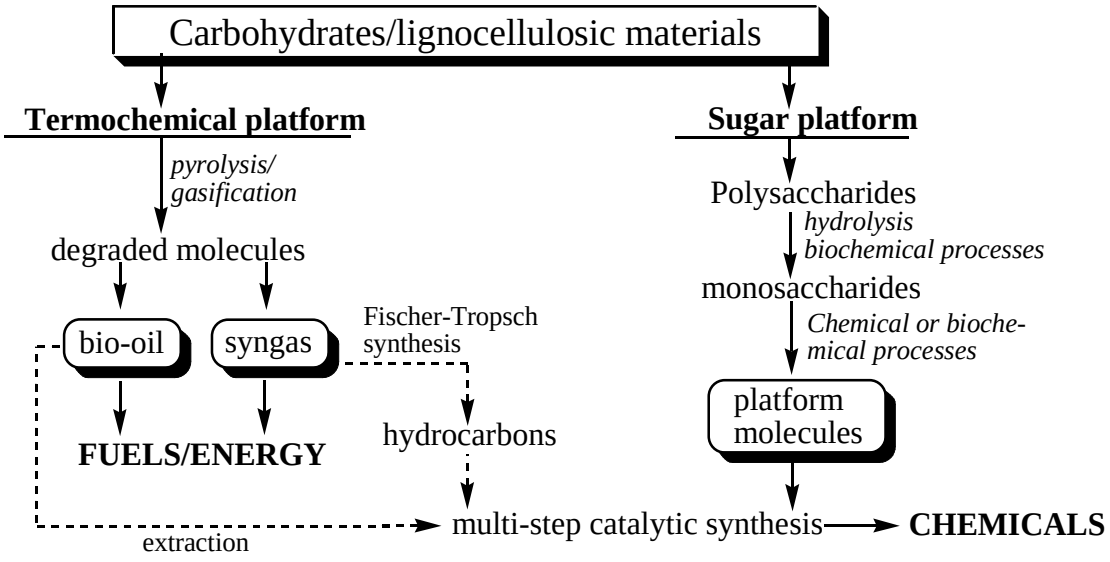


Fig. 3. Process options to produce bioproducts from carbohydrates/lignocellulosic materials taking into account the concept of an integrated LCF biorefinery.[11]

Although the main attention is being focused on carbohydrates, there are other fractions of biomass, like vegetable oils, terpenes, etc., which also should be considered, given their contribution to the synthesis of value-added products.[9,11] Further efforts on the development of specific conversion platforms, e.g. terpenes platform, vegetable oils platform, etc., similar to that for sugars, in order to meet the objectives of an integrated biorefinery of the future, make therefore good sense.[9]

1. Sugars as future biofeedstocks for chemicals generation

Carbohydrates are, beyond their traditional uses in food, lumber, paper, and heat, considered as the main vegetable biomass raw materials with potential to provide industrially and economically viable biobased organic chemicals and materials.[8]

As described above, lignocellulosic materials are composed of nearly 75% carbohydrates, and therefore it is expected that in the near future lignocellulosics will become a potential source of such organic compounds, which will represent the basis to provide biobased alcohols, esters and carboxylic acids, competitive with their petrobased counterparts.[15]

The bulk of the annually renewable carbohydrate biomass is organized in the form of biopolymers, such as cellulose, hemicelluloses, starch, and inulin. However, basic organic chemicals, e.g. alcohols, carboxylic acids, etc., are usually of low molecular weight. Accordingly, the constituent monosaccharides of these biopolymers, namely glucose from cellulose and starch, fructose from inulin, xylose from xylans (hemicelluloses), etc., will ideally be the raw materials for the synthesis of such molecules *via* chemical and/or biochemical processes.[3,8,12]

Thus, for the efficient use of these monosaccharides in an integrated biorefinery system, similar to that shown in Fig. 3, two main challenges have to be met, viz.: (i) the development of efficient and cost-effective hydrolysis processes to break the polysaccharide chains down into the corresponding monosaccharides;[2] and (ii) the design of new catalytic/biochemical routes and processes adapted to the highly oxygenated molecules of monosaccharides, which differ significantly from the non-functionalised hydrocarbon-like compounds of petroleum.[15]

There might also be some advantages in using functionalised monosaccharides, since, in some cases, they will require fewer steps than hydrocarbons (e.g. steps needed to add functional groups, such as -OH, -C=O, -COOH) to produce some basic organic chemicals.[5] The challenge here falls into the development of methods to control the functionality in the final product. As an illustrative example, one can consider the controlled acid-catalyzed dehydration of hexoses and pentoses to produce 5-hydroxymethylfurfural (HMF) and furfural (F), respectively.

As far as carbohydrates are suitable feedstocks for the future chemical industry (biorefineries), a number of platform molecules arising from their conversion have already been identified and considered as potential building blocks for the synthesis of

speciality and fine chemicals needed for nearly all areas of life. In this field, a study carried out by the "National Renewable Energy Laboratory" (NREL) and "Pacific Northwest National Laboratory" (PNNL), has identified twelve valuable sugar-derived building blocks (platform molecules), which are displayed in Table 1.[16] Carbohydrates are thus considered a flexible, but also a challenging class of feedstock to process.

Table 1. Top twelve platform molecules identified by the NREL and PNNL study.

Platform molecule	**Conversion process**
Aspartic acid	biochemical
Glucaric acid	chemical
Levulinic acid	chemical
3-Hydroxybutyrolactone	biochemical
2,5-Furandicarboxylic acid	chemical
Glutamic acid	biochemical
Itaconic acid	biochemical
1,4-Diacids (succinic, fumaric and malic)	biochemical
3-Hydroxypropionic acid	biochemical
Glycerol	biochemical
Sorbitol	chemical
Xylitol/Arabitol	chemical

The potential applications of these molecules as building blocks in the synthesis of specific families of high-value chemicals are very vast, and are well described in the literature.[9] Taking into account the context of this work, special attention will be given to furan monomers as an interesting family of compounds for biobased polymer chemistry. In particular, two first-generation furan derivatives, F and HMF, readily prepared from ubiquitous saccharide sources (Fig. 4), are interesting compounds.[17]

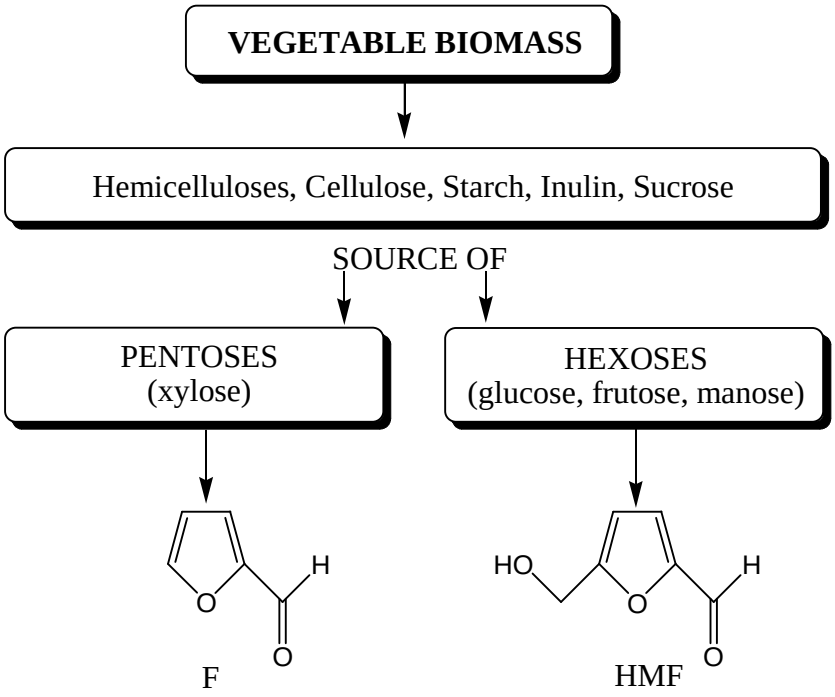


Fig. 4. From vegetal biomass to first-generation furan derivatives F and HMF.[17]

Although they are not enumerated as such, F and HMF could be considered high potential building blocks of the PNNL list, according to the wide variety of value-added compounds arising from their conversion. For F, this exclusion is due to its current large-scale production, whereas for HMF, which is not an industrial commodity so far, its exclusion derives from its instability, so that it should be converted into a more stable compound, such as 2,5-furandicarboxylic acid (FDCA).[18,19] FDCA was selected as one of the top twelve sugar-derived building blocks, and is currently seen as a promising alternative for terephthalic acid (TA) which serves mostly as monomer for poly(ethylene terephthalate) (PET) synthesis.[20,21]

1.1. First-generation furans

1.1.1. Furfural

Furfural is an ‘‘old’’ important molecule firstly obtained in the early 19th century. About a century later it assumed the statute of industrial commodity, and today comprises an industrial production of about 300 000 tons per year.[9,18,19] F can be readily and economically obtained from a wide range of pentosan-rich agricultural and forestry wastes.[18,19]

The industrial production of F firstly involves the hydrolysis of pentosans into aldopentoses, namely xylose and rhamnose. Then, pentoses, in the presence of acidic

catalysts and under high temperatures (200-250 ºC), are progressively dehydrated in a double dehydration process to give a cyclic structure, which loses a water molecule to yields F (Fig. 5).[9,18,19] Though in smaller amounts, 5-methylfurfural is also obtained from rhamnose in this process.

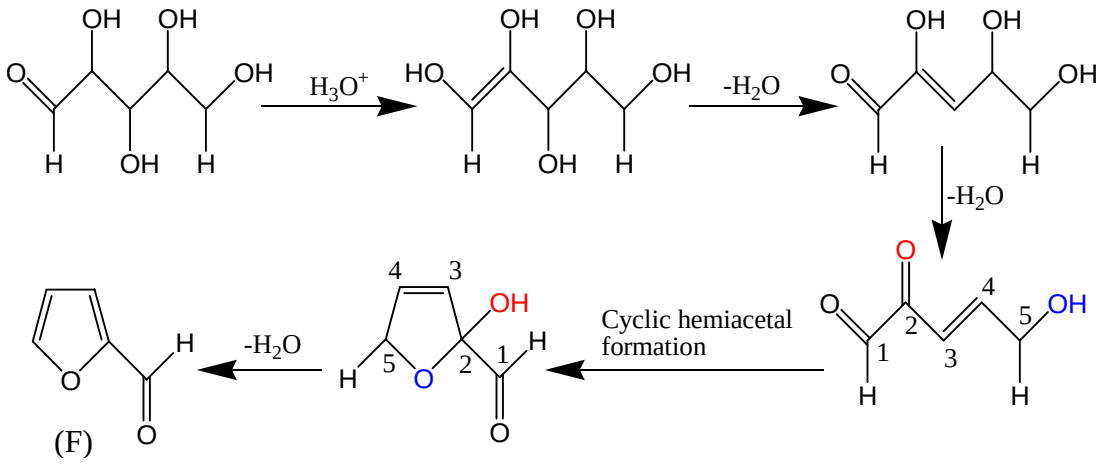


Fig. 5. Illustrative scheme for the production of F from pentoses.[18,19]

About 80% of the F produced worldwide is converted into furfuryl alcohol (FA) by catalytic hydrogenation, which finds a number of applications in chemical industry, mainly in the manufacture of resins, acting as a polycondensation monomer, and as a starting material for the manufacture of tetrahydrofurfuryl alcohol. The remaining part of F is converted into furan, tetrahydrofuran, and many other furan monomers suitable for chain polymerization reactions (see section 1.2, Fig. 9).[9,18,19,21] Since FA serves mostly as polycondensation monomer, it does not belong to that class of F derived monomers mentioned above.

1.1.2. 5-Hydroxymethylfurfural

The synthesis of HMF is carried out from hexoses, e.g. fructose and glucose, through a sequential mechanism identical to that shown in Fig. 5, but ending with HMF.[18,19] Additionally, oligo- and polysaccharides can also be used as HMF sources. In these cases, a hydrolysis step anticipates the mechanism of dehydration proposed for the corresponding monosaccharides. The most convenient and efficient process in terms of chemical yield is the acid-catalyzed dehydration of fructose, which ideally would be obtained from hydrolysis of fructose-containing polysaccharides.[5,18,19,22,23] The dehydration of fructose to HMF can take place *via* acyclic intermediates starting with the formation of an open-chain 1,2-enediol or *via* cyclic/fructofuranosyl intermediates

(Fig. 6).[5] The unsuccess of glucose as starting material can be explained essentially by its high tendency to form a stable six-membered pyranoside structure, limiting thus the enolization step, which is a key step to produce HMF from glucose.[9,17,24]

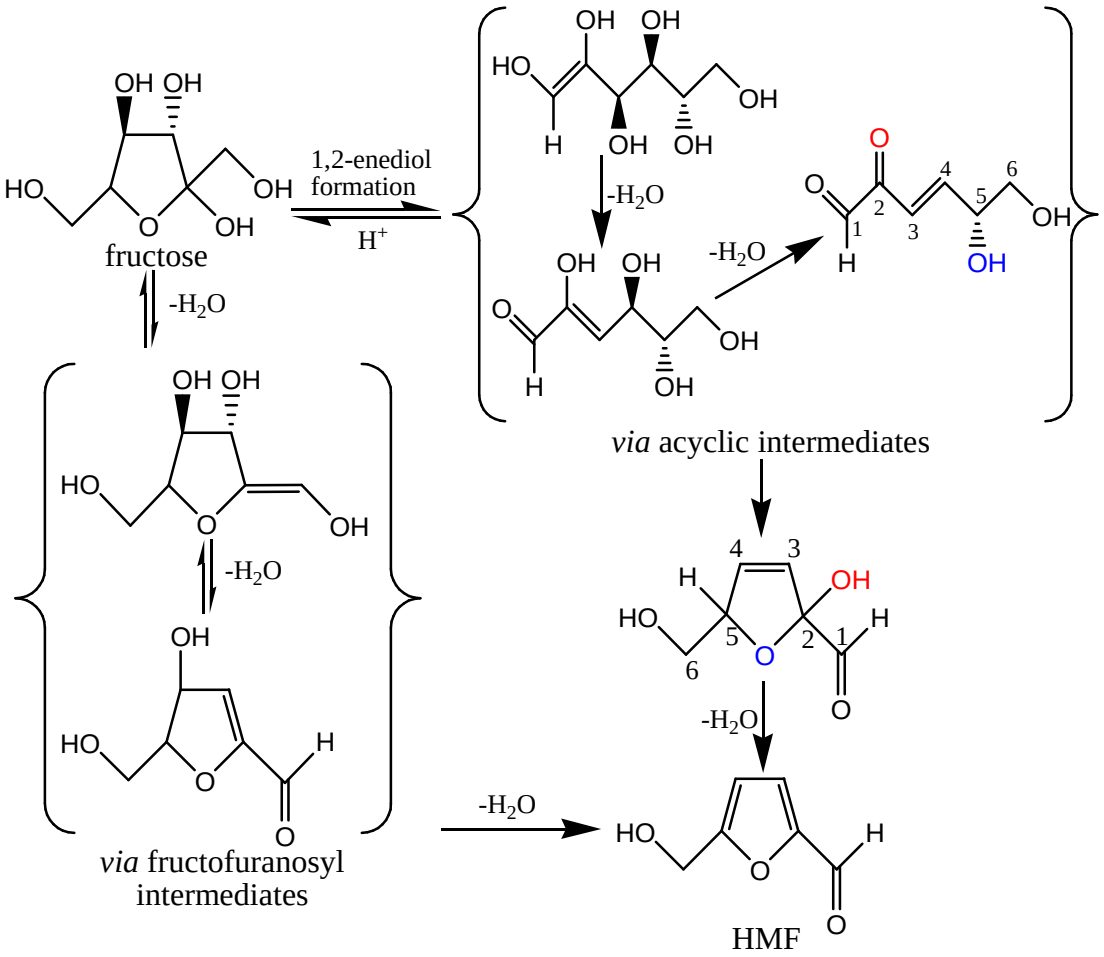


Fig. 6. General scheme for the acid-catalyzed dehydration of fructose to HMF.[5,22]

The dehydration of fructose has been conducted in highly polar solvents, namely water, dimethylsulfoxide (DMSO), dimethylformamide (DMF), and biphasic systems containing water and methyl isobutyl ketone (MIBK), using organic, inorganic, and solid acid catalysts. However, all of these catalytic systems exhibit limitations. Under aqueous acidic conditions, the reactive and unstable HMF molecules are consumed by side reactions, namely rehydration to secundary side products, such as levulinic and formic acid, and self-condensation to form both soluble and insoluble polymeric materials.[5,9,17,23,25]

Even though DMSO prevents the formation of levulinic acid and polymeric residues, the use of this solvent is limited by: (i) the need of energy intensive isolation

procedures to separate DMSO; and (ii) the possible formation of toxic S-containing by-products from its decomposition.[9,17,22]

Although fructose has been the main feedstock to prepare HMF in optimal yield, the large-scale production of HMF will require glucose as feedstock, since it is a more abundant and inexpensive monosaccharide. In the last few years, a number of publications have reported the use of different catalytic systems in ionic liquids to convert glucose to HMF.[24,26-28] Furthermore, some of these works dealt with the direct conversion of cellulose into HMF, which is a more interesting process from an economical point of view.[24,26,27] Such conversion inevitably requires hydrolysis of cellulose down to glucose, as well as isomerization of glucose into fructose which until now was seen as a limiting step in the conversion of glucose into HMF.

In this sense, a recent study is likely to be previleged.[24] This work shows that is possible to convert cellulose directly to HMF in the presence of metallic chlorides-type catalysts, namely $CrCl_3$, in ionic liquids, as well as the possibility of isomerization of glucose to fructose (Fig. 7). When coordinated with $(CrCl_{3+n})^{n-}$ complex, the 1,4-glycosidic bonds get weaker, becoming thus more vulnerable to water attack, a phenomenon that leads to the successful hydrolysis of cellulose into glucose and corresponding oligomers. Then, glucose is isomerized to fructose *via* Cr(III)-enediol complex intermediate. Fructose is then dehydrated to HMF through a sequential mechanism identical to that shown in Fig. 6. Additionally, the enediol can follow that acyclic intermediates route shown in Fig. 6 to yields HMF.

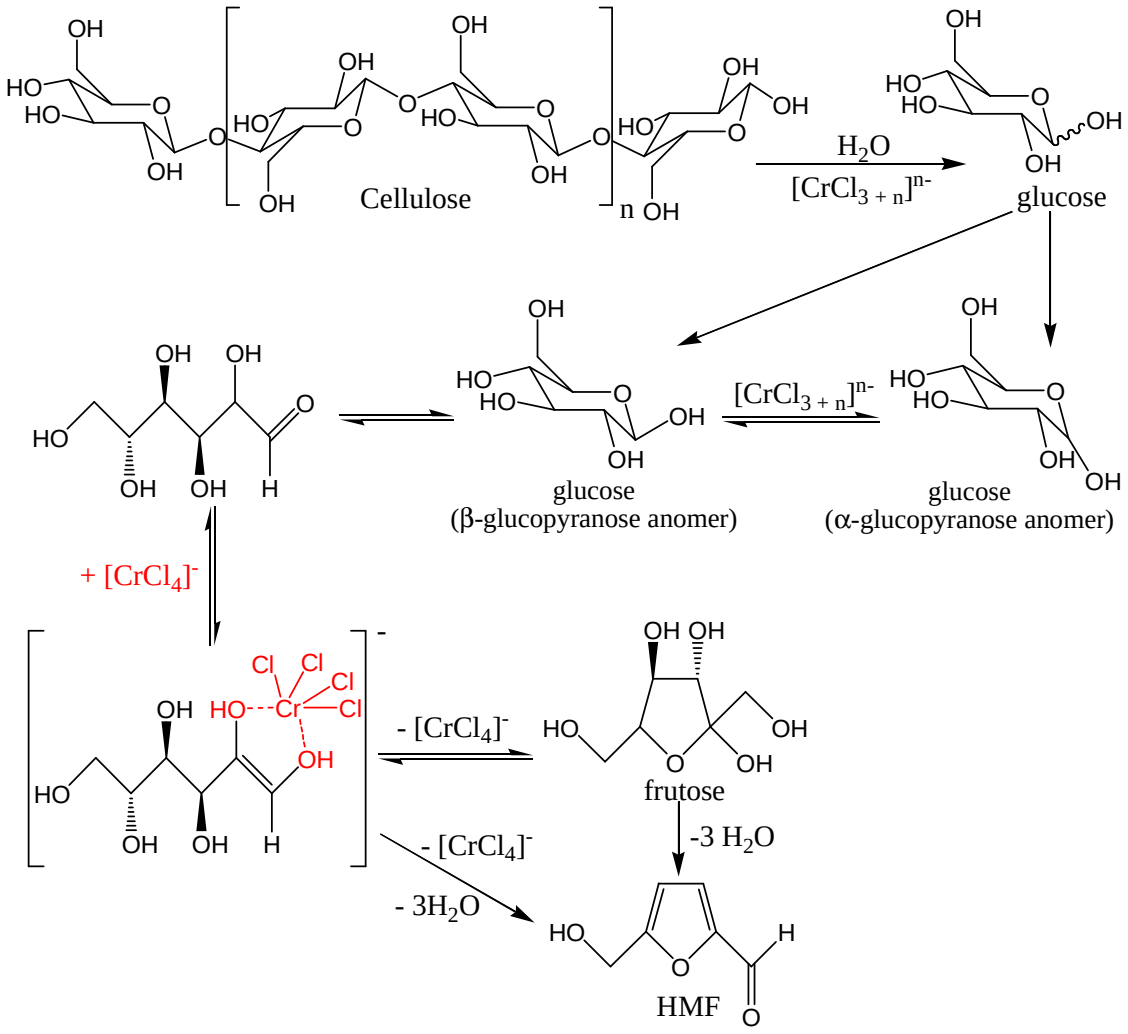


Fig. 7. Direct conversion of cellulose to HMF catalyzed with CrCl3 in (C4mim)Cl.[24]

According to the growing interest in preparing HMF from cellulosic materials, and the vast amount of recent work being published on this context, it seems quite obvious that an efficient and cost-effective approach may soon become a reality. Both the overall high costs of the processes and the non-green systems used, are still the main reasons for not preparing HMF through sugar routes.[9]

In these circumstances, most of the HMF commercially available is produced by using furfural as starting material as described by Moreau *et al.*[29] This route involves first the protection of the carbonyl group of F in the form of a dithiolane heterocycle, followed by the hydroxymethylation of C-5 with aqueous formaldehyde and subsequent deprotection of the carbonyl group to yields HMF (Fig. 8).

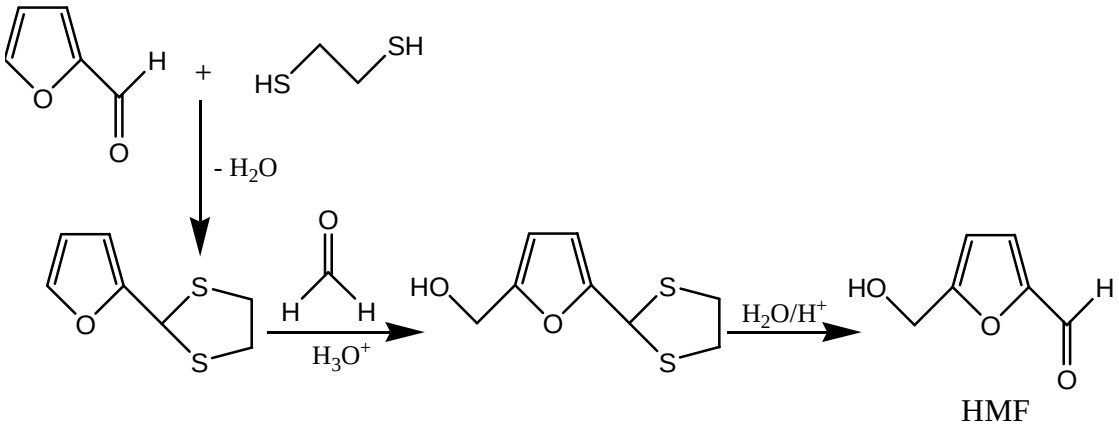


Fig. 8. General synthetic pathway to prepare HMF from F.

HMF is currently seen as one of the top biobased platform molecules, and it is called a ‘‘sleeping giant’’, mostly due to its potential as precursor of useful 2,5-disubstituted furan monomers for polymer applications (see section 1.2, Fig. 10),[5,9,21,28] of which, those with higher industrial potential are FDCA, 2,5-bis(aminomethyl)furan and 2,5-bis(hydroxymethyl)furan (BHMF) (a, b and c in Fig. 10 respectively).[9,17] Furthermore, HMF could serve as an excellent source of biofuels, since it can be converted to 2,5-dimethylfuran *via* selective hydrogenation, which has been shown to be an excellent biofuel .[5,24,30-33]

1.2. Furan derivatives for polymer applications

The emerging interest in furan derivatives for polymer applications is a result of their specific characteristics closely associated with the peculiar behaviour of the furan heterocycle, particularly its mixed aromatic-dienic character, which opens vast perspectives for the production of polymeric materials.[18,19]

When compared with benzene and its homologous, e.g. pyrrole and thiophene, furan has the lowest aromatic and the highest dienic character. The predominance of the dienic character is putting some monosubstituted furan derivatives on the way of new approaches in macromolecular synthesis and modification, namely through Diels-Alder (DA) reaction, where furan ring plays the role of dienic reagent with a variety of dienophiles, e.g. maleiamides.[21,34,35] This may represent a starting point for the preparation of polymeric materials with novel properties and applications.

Moreover, difunctional furan derivatives, namely 2,5-disubstituted furans, are suited precursors of condensation polymers, among which polyesters, some of them

being the furan version of the most commercialized polymers worldwide (viz. PET, poly(butylene terephthalate) (PBT) and poly(propylene terephthalate) (PPT)).[17,20,36]

This wide scope of polymeric materials is quite dependent on the two first-generation furans (F and HMF), which can be converted into two distinct large families of monomers that may, in the future, simulate those presently available from petrochemistry.[18-21,36]

The first family (Fig. 9) includes structures derived from F by linking various vinyl moieties and acrylic or epoxide (oxirane) groups to the heterocycle, which can be polymerized or copolymerized by chain reactions, e.g. free radical, anionic, and cationic polymerizations, through these external moieties.

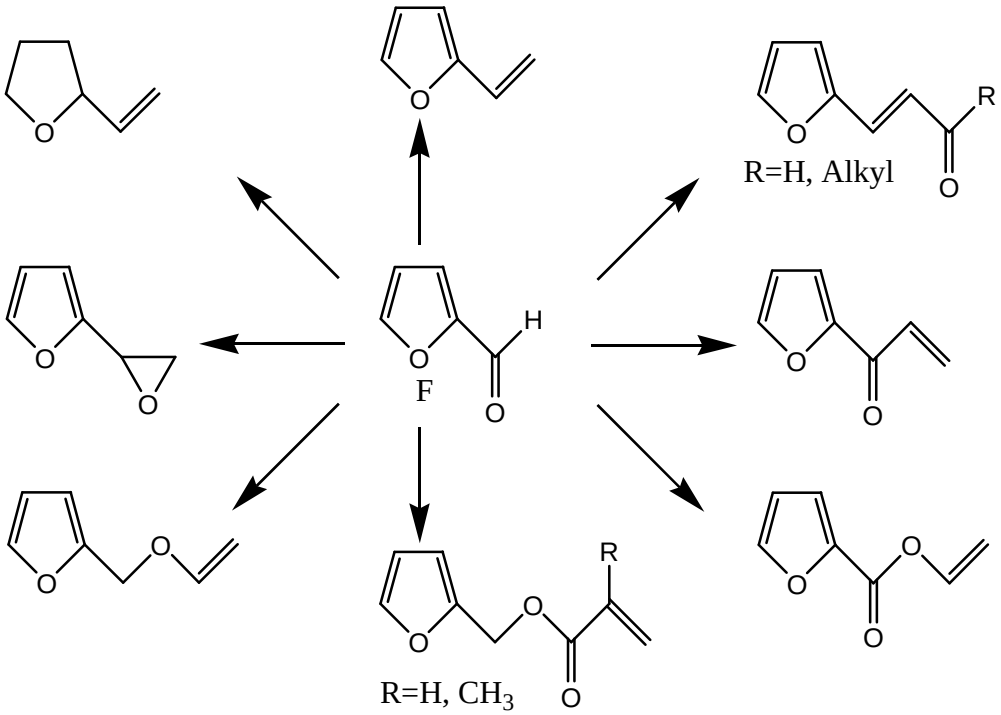


Fig. 9. Furan monomers derived from furfural (F).[21]

The second family (Fig. 10) includes structures derived from HMF by linking carboxyl, hydroxyl, amino or isocyanate functions, to the heterocycle, which are molecules suited for step-growth reactions. Whereas the monomers shown in Fig. 9 give rise to polymerized or copolymerized structures with the heterocycle pendant on the backbone, the monomers shown in Fig. 10 give rise to polycondensation structures with the furan heterocycle being part of the backbone.[19]

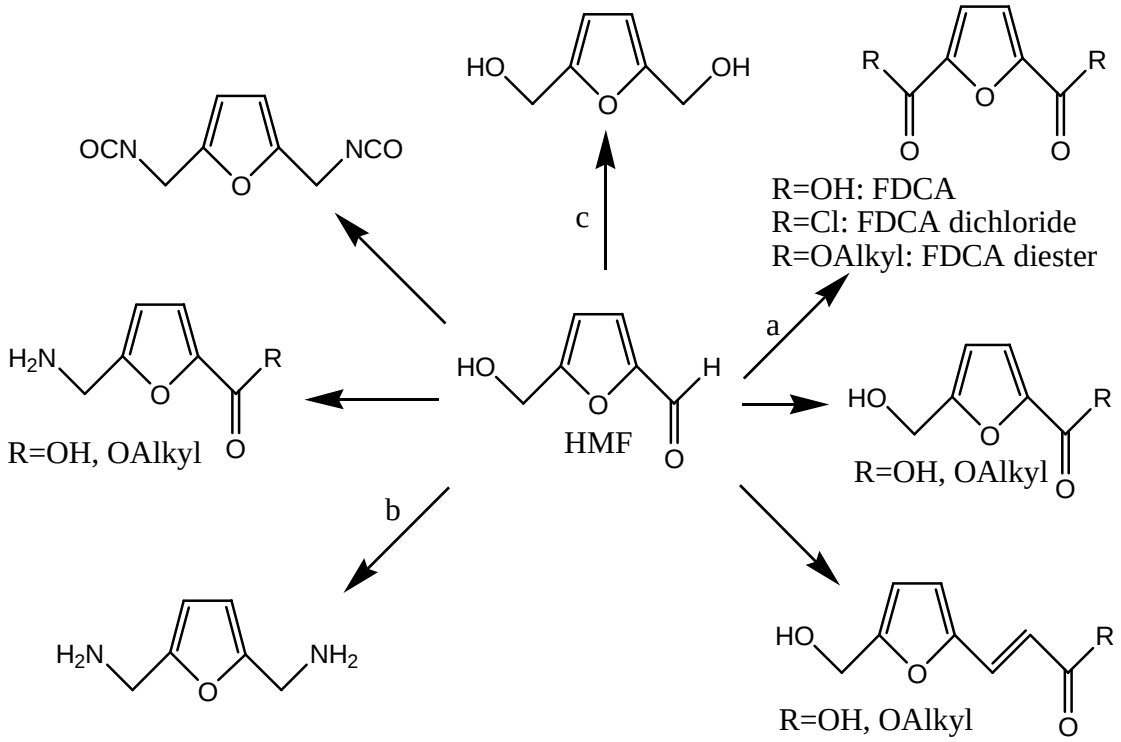


Fig. 10. Furan monomers derived from 5-hydroxymethylfurfural (HMF).[21]

Additionally, F derivatives can also be used as precursors of difunctional difuran monomers suitable for step-growth polymerizations. Their synthesis is based on the acid-catalyzed condensation of the corresponding 2-substitued furan derivatives in the presence of an aldehyde or ketone as shown in Fig. 11.[19,21]

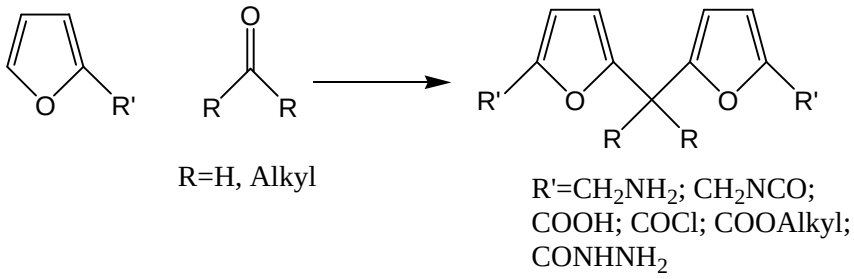


Fig. 11. Difuran monomers arising from F derivatives.[19,21]

Among all of these monomers, FDCA and its derivatives (Fig. 10), namely its corresponding esters (R=OAlkyl) and its dichloride (R=Cl), constitute the most interesting family of precursors in the synthesis of 2,5-disubstituted furan polyesters and therefore the most obvious given the context of this work.

1.2.1. 2,5-Furandicarboxylic acid

As described before, FDCA is one of the most interesting chemicals derived from HMF, mostly due to its potential for replacing petrobased acids in polymer applications, such as TA (as well as isophthalic and adipic acids) in the synthesis of polyesters. Furthermore, FDCA can also be used in the synthesis of polyamides.[9,17,18]

The synthesis of FDCA by the oxidation of HMF using conventional oxidants, such as nitric acid, has been reported.[37] However, it seems that oxidation of HMF is not completely selective to FDCA and significant amounts of byproducts are also formed.[9,17] The best results are obtained with heterogeneous oxidation systems with noble metal catalysts, namely platinum supported on either carbon or alumina (Pt/C or Pt/Al) in water under oxygen pressure.[9,17] However, it seems that high catalyst-to-substrate ratios in the order of ~ 1:1 by weight are required.[38]

The synthesis of FDCA directly from fructose would be the most interesting route to obtain FDCA. In this sense, a promising route was reported.[39] This route involves the catalytic one-pot cyclization and oxidation of fructose over bifunctional acidic and redox catalysts, namely cobalt acetylacetonate encapsulated in sol-gel silica. Following this approach, fructose was selectively converted into FDCA (selectivity of 99% and 72% of conversion of fructose) in a yield close to 70% at 165 ºC and 2-MPa air pressure.[39]

However, the most recent studies deal with the synthesis of FDCA from HMF using heterogeneous catalytic systems, such as gold nanoparticles.[38] By using water as solvent, air as oxidant, and under mild conditions (65-130 ºC, 10 bar), it was found that one-pot synthesis of FDCA from HMF can be successfully achieved with gold nanoparticles supported both on nanoparticulate cerium oxide (Au-CeO_2) and titanium oxide (Au-TiO_2) as catalysts (Fig. 12).[38]

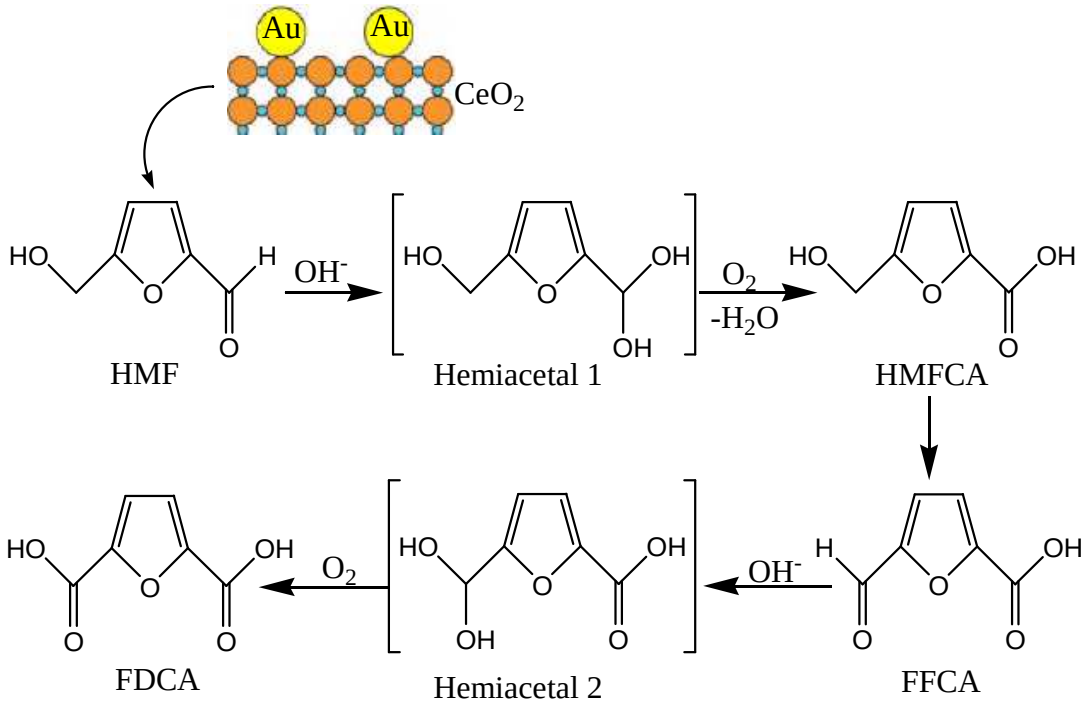


Fig. 12. Reaction pathway for aqueous aerobic oxidation of HMF into FDCA catalyzed by Au-CeO_2.[38]

As a building block in polymer synthesis, FDCA has the versatility to be converted into a number of derivatives through characteristic reactions of the carboxylic acid group. For example, dimethyl 2,5-furandicarboxylate (DMFDC) can be obtained by acid catalyzed esterification of FDCA with methanol, and 2,5–furandicarbonyl dichloride (FDCDCl) by reacting FDCA with thionyl chloride ($SOCl_2$) (Fig. 13).[21,40]

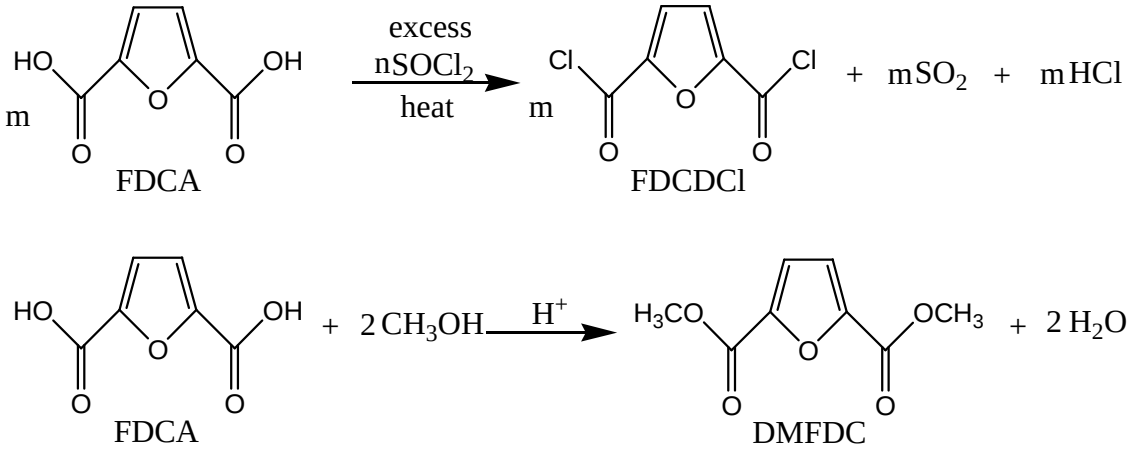


Fig. 13. Reactions of formation of FDCDCl and DMFDC from FDCA.[40]

2. Polyesters

The family of polyesters includes all polymers with ester groups in the backbone, i.e. ester linkages in the main chain, and therefore holds a huge diversity of materials, as a result of the broad range of structural units connecting the ester groups. Polyesters find a vast number of applications in diverse areas of our modern life, including bottles for soft drinks and water, fibers for textile industry, photographic films and recording tapes, etc., thus reflecting the high versatility of such materials.[41,42]

In section 1, the state of the art on furan derived polyesters, and particularly FDCA derived polyesters, will be given. However, before that, the focus will be on the synthesis of polyesters.

2.1. Synthesis of polyesters: Step-growth polymerization

Linear polyesters are typically synthesised by step-growth polymerization processes, by using difunctional monomers of the AB type, i.e. hydroxy acids, or by combining AA and BB difunctional monomers, i.e. diols and dicarboxylic acids respectively. Due to the formation of water as byproduct these polymerization reactions are also known as condensation polymerization or even polycondensation.[42]

The theory of step-growth polymerization is mainly based on the pioneering work of Carothers[43] and on the theoretical contributions of Flory.[44] According to this theory, the definition of polycondensation is based on two aspects: (i) continuous elimination of a small byproduct (e.g. H_2O, HCl, etc.) in every propagation step to promote the displacement of the equilibrium towards the production of high-molecular-weight chains, and (ii) the reactivity of the endgroups is independent of the chain length and all of the reactive species can react with each other at any given time. In this sense, assuming that water (or other small product) is removed as it is formed, and therefore no equilibrium is established, the polymerization proceeds in this way: (i) the initiation involves the reaction of two difunctional monomers to form dimers and (ii) the propagation involves first the dimers reacting with both the monomers and themselves to form trimers and tetramers respectively, and then the trimers and tetramers reacting with themselves, with each other, and with the monomers and dimers, continuing in this stepwise manner, until finally long-chain polymers are obtained.[45,46] The increase of the chain lengths with conversion obey the ‘‘Carothers equation’’ (1),[46] which relates the degree of polymerization (DP) with the extent of the reaction (p):

$$\overline{DP} = \frac{1}{1 - p} \quad (1)$$

From this equation one can conclude that high molecular weight materials will only be achieved for very high conversion values (>98-99%). A requirement for this equation to be valid is the use of a stoichiometric mixture of monomers, which on the one hand is readily achieved when using purified AB difunctional monomers, but on the other hand presents a practical problem when using AA and BB difunctional ones.[42,45]

From the diverse synthetic condensation polymers prepared in the course of a series of pioneering investigations realized by Carothers and his team in the mid 1920s, polyesters were the first family prepared.[42,43] By using a vast number of combinations of aliphatic diacids with aliphatic diols, this work dealt with the preparation of several polyesters.[42,43]

The first commercialized polyester was PET in the early 1950s.[41] Its industrial production is still based on melt polycondensation (melt-transesterification polymerization), using either TA or its dimethyl ester with ethylene glycol (EG) as diol.[47] Other commercial polyesters, such as PBT and PPT, are also prepared *via* the same routes, but using different diols as comonomers, viz. 1,4-butanediol (BDO) and 1,3-propanediol (PDO), respectively.[47]

2.1.1. Polycondensation methods

There are numerous methods of polycondensation, among which are melt polycondensation, solid-state polycondensation, solution polycondensation, and interfacial polycondensation. Polyesters can be prepared by each of these methods depending on their finality and the nature of the monomers.

2.1.1.1. Melt polycondensation

Melt polycondensation is a two-stage polymerization process, which can be employed by following either of these routes: (a) *via* transesterification of a diacid dimethyl ester with a diol to form a diester, which is the monomer for polycondensation reaction; or (b) *via* direct esterification (Fischer esterification) of a diacid with a diol to yields the diester monomer; both of them followed by polycondensation (Fig. 14).[47]

1st Stage: Synthesis of the polymerizable bis(hydroxyalkyl)esters step

a) Transesterification of the diacid dimethyl ester with an excess of diol, in order to obtain oligomeric structures of the bis(hydroxyalkyl)esters type with alkyl = ethyl, propyl, butyl, etc., depending on the diol used. This reaction is usually carried out at temperatures ranging from 150 to 210 ºC under a stream of dry nitrogen which ensures the rapid evaporation of the byproduct (methanol) as it is formed, thus allowing the equilibrium to be continuously displaced towards the bis(hydroxyalkyl)ester formation. This stage ends when distillation of both the released alcohol and the excess of diol stop, which is ensured by applying a high vacuum to the system and slightly increasing the temperature (these two steps are also associated with the beginning of the 2nd stage);

b) Direct esterification (Fischer esterification) of the diacid with an excess of diol in the presence of a mineral acid as catalyst at high temperatures (240-270 ºC). Water, the by-product formed during the reaction, should be removed to ensure that the reaction is as complete as possible. This stage ends in a similar way to that described for a).

2nd Stage: Polycondensation step: the polymerization of the bis(hydroxyalkyl)ester oligomers, prepared either *via* a) or b), takes place by gradually increasing the temperature from 200 to 280 ºC with continuous withdrawal of the released diol by evaporation under vacuum (~100 Pa, the same applied at the end of the 1st stage). The overall reaction time, including both stages, generally ranges from 5 to 10 hours.[47,48]

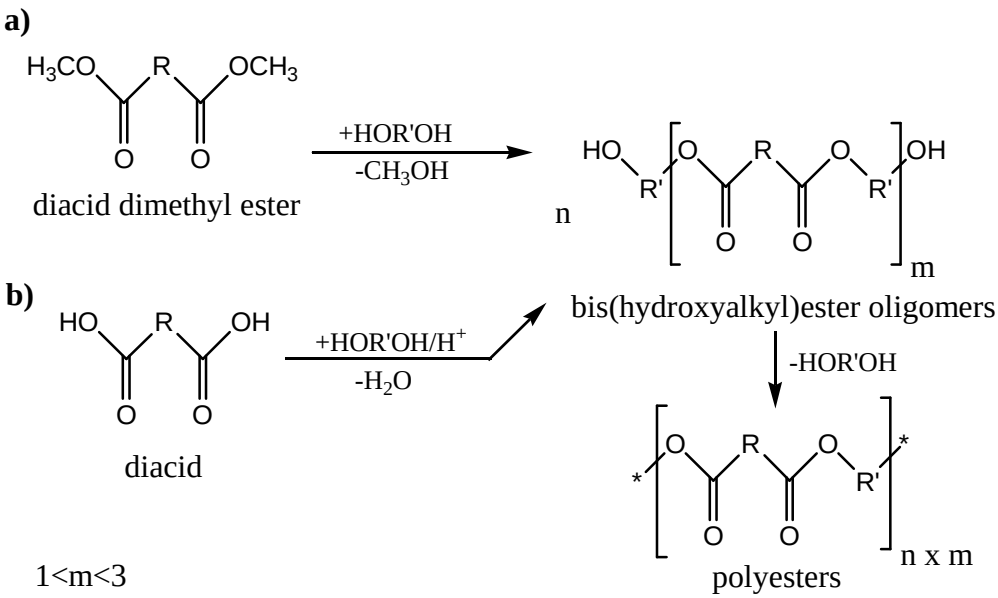


Fig. 14. General reaction pathways for the synthesis of polyesters by melt polycondensation.[47,48]

The melt polycondensation process starting *via* a) may be used as a logical alternative to that starting *via* b), since the completion of the formation of bis(hydroxyalkyl)ester species can be accelerated by an easier withdrawal of methanol when compared to water, thus making the formation of pure diester oligomers much simpler.

Melt polycondensation is by far the most used polymerization method for preparing polyesters mostly due to its simplicity, since it involves only the reactants, choice of catalysts and the control of variables such as temperature and pressure.[45] Additionally, the separation of the formed polymer is simple since no solvents are used and the amounts of catalysts are very small.[45,48] However, for melt polycondensation to be successful, the monomer, oligomer, and even the polymer must withstand temperatures near or above 200 ºC for several hours, unless diols with very low boiling points are used and therefore the excess of diol can be removed at lower temperatures.

Since the reaction temperature must be in accordance with the boiling point of the diol, the use of diols with high boiling points, e.g. aromatic diols, is not common in melt polycondensation processes. In general, aliphatic diols are suited for melt polycondensation, so that PET, PBT, etc., are prepared by this method.

2.1.1.2. Solution and interfacial polycondensations

The exploitation of polycondensation processes allowing the use of mild conditions can extend the realm of diols to be used and therefore the realm of polyesters, since both the non-volatile diols that require high temperatures to be processed by melt polycondensation and the diols unstable at high temperatures can be processed at lower temperatures (ranging from 0 to 50 ºC) by solution and interfacial polycondensations, by using the faster Schotten-Baumann reactions of acid chlorides (Fig. 15).[45,49] Thus, polyesters may be produced by replacing the diacid or diester reactants by the corresponding dichloride.

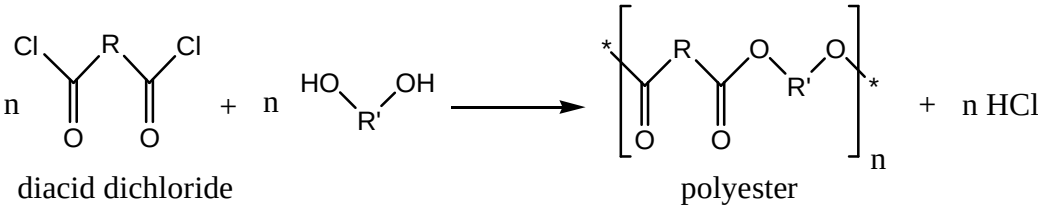


Fig. 15. General reaction scheme related to solution and interfacial polycondensations.[21]

Solution polycondensation is carried out at room temperature in an inert solvent, e.g. tetrachloroethane (TCE), for the reactants and polymer. The reaction is generally catalyzed through the introduction of a proton acceptor, e.g. pyridine, which ensures the neutralization of HCl and therefore the achievement of a continuous non-equilibrium state.[45,49,50] Keys to success of the reaction are cooling (to about 0 ºC) just after placing the diol solution into the reaction flask, and gradual addition of the diacid dichloride solution to the stirred diol solution (after the addition of the dichloride, the polymerization takes place at room temperature).[49,50] Solubility of the polymer during the polymerization is also fundamental to ensure attainment of high molecular weight polymers. In this sense, the use of tetrachloroethane has shown good results.[21]

Interfacial polycondensation is quite different from the usual step polymerization processes, i.e. melt and solution polycondensations. In the former, the monomers diffuse to the interface and undergo polymerization there, reacting only with the growing polymer chain ends. The interface occurs between two liquid phases, i.e. organic and aqueous phases, containing the diacid dichloride and the diol, respectively. Normally, the aqueous phase contains a 100% excess of an alkali, such as NaOH, to ensure total dissolution of the diol, an essential feature to obtain long chain polymers.[50] The alkali acts also as a neutralization agent to the HCl formed during the polymerization, thus avoiding the use of an additional proton acceptor.[45,49,50] An additional key to success is the use of an organic solvent capable of dissolving both the diacid dichloride and the polymer. In this sense, dichloromethane (DCM) has often been used.[21,49]

Aromatic polyesters are generally prepared by these two methods. However, phenols are particularly suited for interfacial polycondensation and, in fact, those polymers prepared from phenols and diacid dichlorides by the interfacial method have higher molecular weights than those prepared in solution.[49,50] The solution method may, however, be used as an alternative to the interfacial method in cases where phenols do not readily dissolve in the alkaline aqueous solution.[50]

2.1.1.3. Solid-state polycondensation

Polyesters prepared by melt polycondensation can undergo further polycondensation in the solid state, known as solid-state polycondensation (SSP), using temperatures between their glass transition temperature (Tg) and crystalline melting point (Tm), in order to increase their chain length.[51-53] First, a prepolymer is prepared by

the polymerization processes described before. Then, by increasing the temperature, the prepolymer is solid-state polymerized to higher molecular weights, with continuous elimination of the byproduct. This is due to the fact that temperatures used in SSP allow the end groups of the prepolymers to be mobile enough so they can react. SSP involves mostly two reactions occurring simultaneously, viz.: (a) the transesterification reaction between two hydroxyalkyl ester end groups; and (b) the transesterification reaction between a methyl ester/carboxylic acid end group and a hydroxyalkyl ester end group (Fig. 16). The byproducts, e.g. diol and methanol/water, are removed by passing a stream of an inert gas, such as nitrogen, through the system or by maintaining the system under vacuum.[51-53]

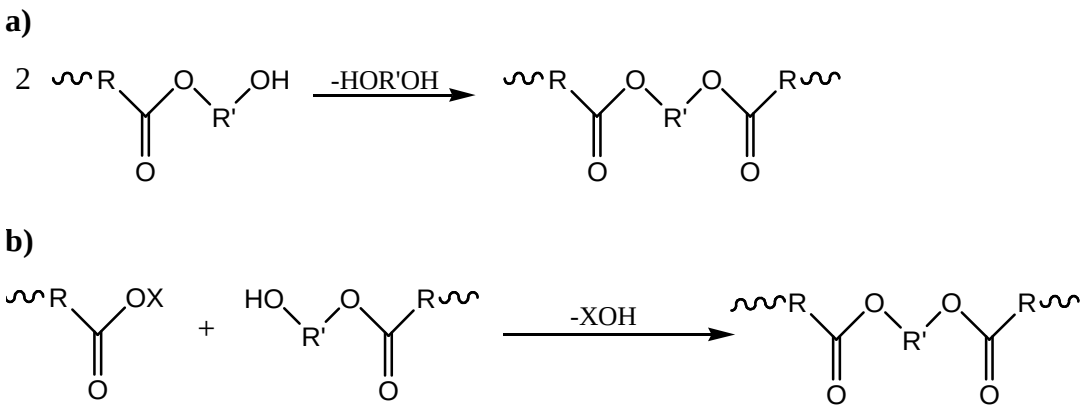


Fig. 16. Reaction schemes for SSP of melt polycondensation polyesters.[53]

SSP can therefore be seen as a subsequent step to the common melt polycondensation process, leading to higher molecular weight (>30,000 g/mol) polyesters, e.g. PET and PTT, required for applications such as injection molding.[51,52] Polyesters prepared by melt polycondensation, e.g. PET and PTT, have a number average molecular weight of 15,000-25,000 g/mol, and, as a result, are used for applications that do not require high molecular weight polyesters, such as fibers for the textile industry.[51,52]

3. Furan derived polyesters

The realm of furan polyesters has been the subject of many studies, beginning some thirty years ago with the work carried out by Moore and Kelly, who for the first time established the relation between reactivity and structural characteristics of various furan monomers and the properties of the corresponding polyesters, using 2,5-furandicarboxylic acid derivatives (as well as 2,3-, 2,4-, 3,4-furandicarboxylic acids) reacting with aliphatic and aromatic counterparts, such as 1,6-hexanediol and bisphenol A, to give furan-aliphatic and furan-aromatic polyesters respectively, as well as with furan and tetrahydrofuran diols to give fully furanic polyesters.[54-59]

Poly(hexamethylene 2,5-furandicarboxylate) (PHMF), is an example of a furan-aliphatic polyester, whose synthesis was based in the melt polycondensation process *via* transesterification of DMFDC with 1,6-hexanediol using a mixture of calcium acetate ($Ca(OAc)_2$) and antimony oxide (Sb_2O_3) as catalysts (Fig. 17).[55,56]

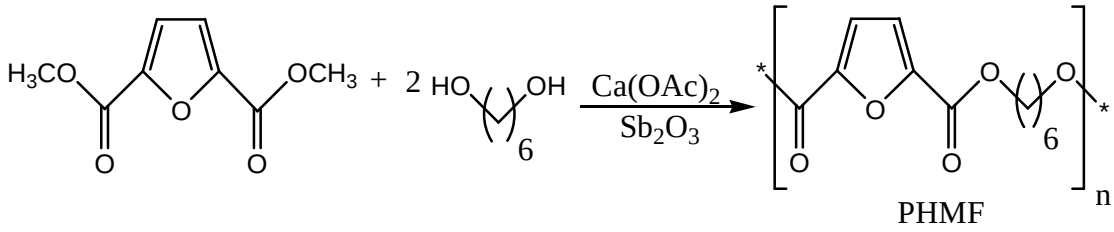


Fig. 17. Synthesis of PHMF by melt polycondensation.[56]

The synthesis of furan-aromatic polyester, poly(4,4'-isopropylidenediphenylene 2,5-furandicarboxylate) (PIPDPF), from combining FDCDCl with bisphenol A, was carried out by both solution and interfacial polycondensations (Fig. 18). The best result was achieved in chloroform, at room temp, using triethylamine as the acid acceptor. A white polymer with an intrinsic viscosity of 0.5 was obtained in 90% yield.[58]

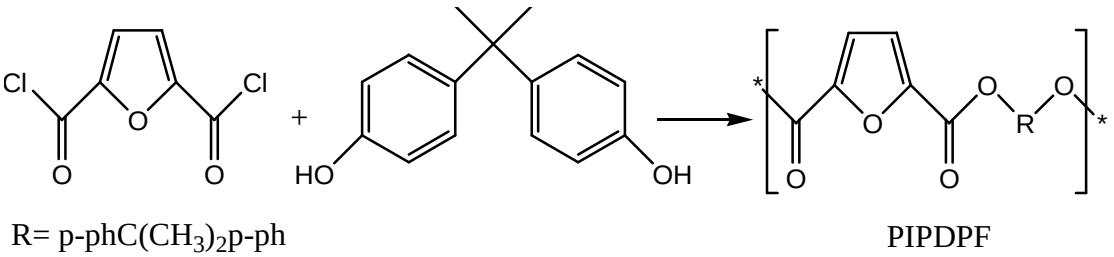
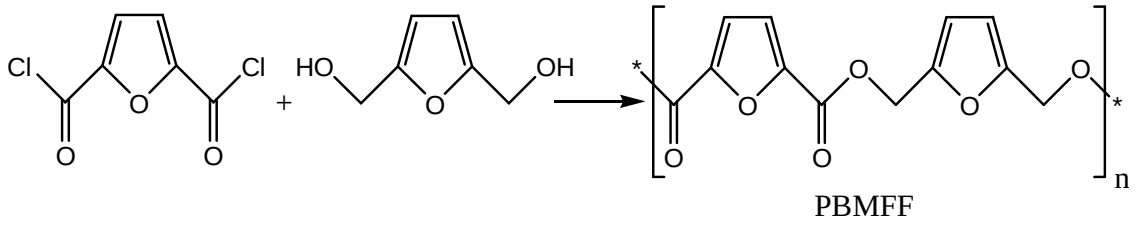


Fig. 18. Synthesis of PIPDPF.[58]

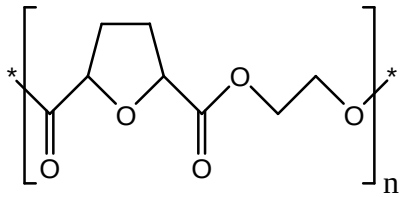
The synthesis of fully furanic polyesters, such as poly(2,5-furandimethylene 2,5-furandicarboxylate) (PFDMF), using BHMF and FDCDCl as monomers (Fig. 19), was carried out by polycondensation in solution, using various solvents (of which chloroform was chosen as the most useful). For all the experiments, only low viscosity (<0.12) polymeric materials were obtained.[56]



PBMFF

Fig. 19. Synthesis of PFDMF.[56]

According to the modest information obtained on DPs, the conclusions on this point were reflected only by the intrinsic viscosities, which suggested low DP values for all of these polymeric structures. Furthermore, excepting the PHMF and identical polyesters, including poly(ethylene 2,5-tetrahydrofurandicarboxylate) (PETHF) (Fig. 20), none of the polyesters discussed above exhibited well-defined melting transitions. PETHF exhibited a melting transition at 150 ºC which was found to be reproducible on cooling and reheating.[55,56]



PETHF

Fig. 20. PETHF structure.[55,56]

Thermal analysis also suggested different degradation behaviors for these polyesters. Whereas the furan-aromatic polyesters (e.g. PIPDPF) were quite resistant to heat, the furan-aliphatic and fully furanic structures displayed marked lower thermal stability. PIPDPF showed no transitions till about 240 ºC. The melting of its crystalline domains started at ~320 ºC and was accompanied by low weight loss.[55,58]

Hirai *et al.*[60] have studied a new class of furan polyesters to date, viz., polyesters prepared from 5-hydroxymethyl-2-furoic acid (HMFA) (Fig. 21). However, only linear

and cyclic oligomers with DPs_{max} = 6 were obtained by treating HMFA with piridinium salts at 60 ºC, and a black intractable resinous product when HMFA was polymerized by melt polycondensation.[18,60]

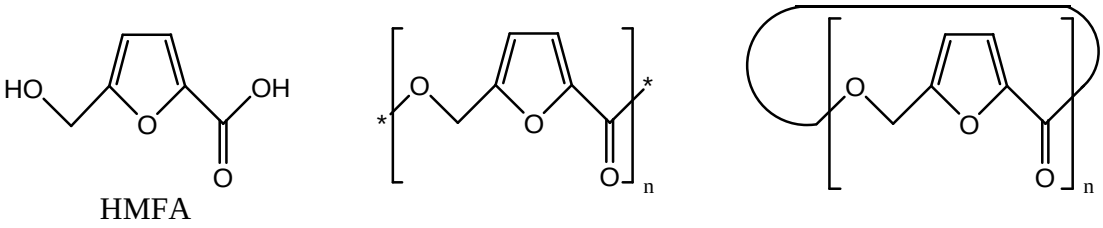


Fig. 21. HMFA and both linear and cyclic oligomers arising from its polymerization.[18]

Roudet and Gandini[18] studied polyesters from similar structures to the previous hydroxyacid with an intermediate unsaturation, viz. ethyl 5-hydroxymethyl-2-furanacrylate (EHMFA). Polycondensation of EHMFA promoted by $KHCO_3$, was found to be an interesting route to the corresponding polyester (Fig. 22). Both from solution and melt polycondensation the polymer was found to crystallize out of the reaction medium, resulting in structures with DP values of about 20. Regular structures were obtained, which showed to be stable up to 280 ºC.

This polymer was also interesting due to the fact it could be further transformed through the reaction of the exocyclic double bonds present in each monomer unit. In fact, upon irradiation with UV light, the polymer crosslinked through a classical photocycloaddition mechanism (Fig. 22).[18]

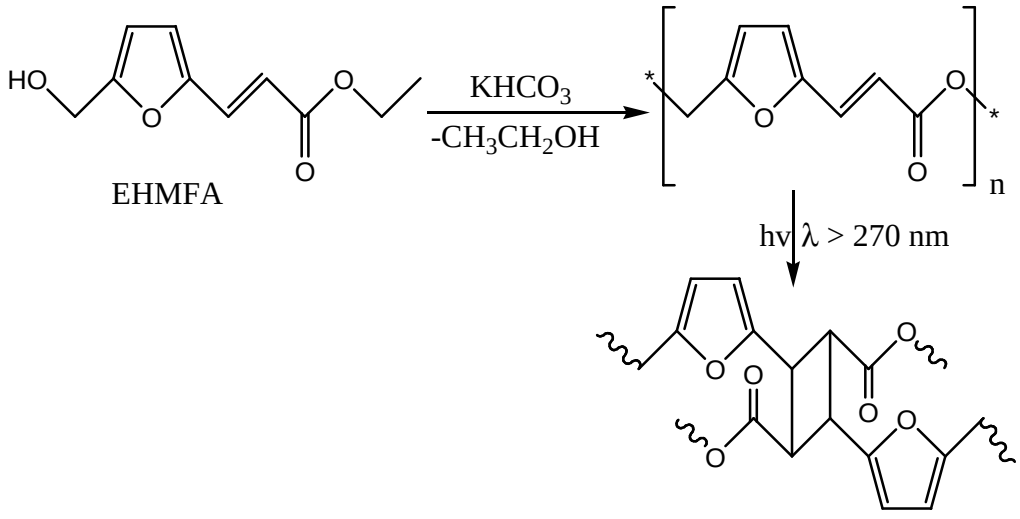


Fig. 22. Polycondensation of the hidroxyester EHMFA and further crosslinking.[18]

More recently, Gandini and coworkers synthesized and characterized several photosensitive furan compounds incorporating acrylate functions at C_2 of the ring.[61] Then, the synthesis and characterization of copolymers of EHMFA and aliphatic hydroxyesters such as ethyl-6-hydroxyhexanoate (EHH) (Fig. 23) was reported.[62] These structures are photosensitive and therefore capable to form crosslinked products when exposed to near-UV irradiation, suggesting their possible use as photoresists, for example in offset printing plates.[62]

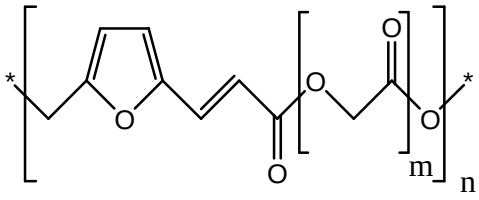


Fig. 23. Copolyester from polycondensation of EHMFA with EHH.[62]

An interesting addition to the realm of FDCA derived polyesters is the Storbeck and Ballauff's work,[63] which dealt with polyesters fully derived from renewable resources, i.e. carbohydrates. These polymers were prepared from FDCDCl and the three isomers of 1,4:3,6-dianhydrohexitols (viz. isosorbide, isomannide, and isoidide) (Fig. 24), by polycondensation in solution at low temperatures, using TCE as solvent and pyridine as proton acceptor, and then isolated by precipitation in methanol. Their molecular weights were between 9,000 and 25,000 and regular structures were suggested by both elemental analysis and ^{13}C and ^{1}H Nuclear magnetic resonance (NMR) spectroscopy. The high macromolecular stiffness and thermal stability of these materials were also suggested, the former by Tg values around 180 ºC and the latter by the absence of weight loss below 320 ºC. However, despite the structural regularity, no mention of crystallinity or of melting features was made.[63]

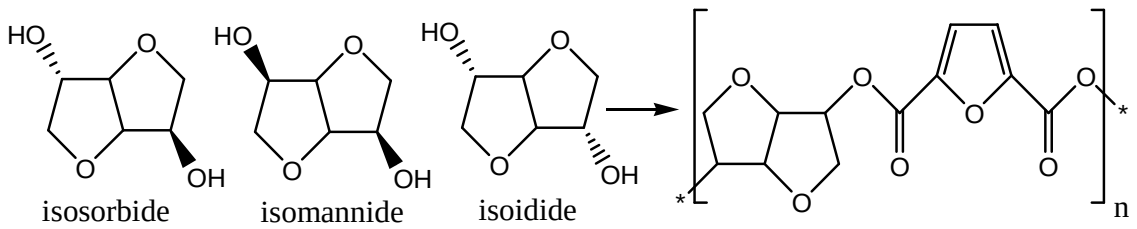


Fig. 24. Structure of 1,4:3,6-dianhydrohexitols and polyesters resulting from their combination with FDCDCl.[63,64]

Finally, a new class of furan polyesters arising from the combination of difuran-carboxylic derivatives (Fig. 25), e.g. diacid diesters and dichlorides, with a wide number of aliphatic, aromatic and furan diols, was reported in the late 1990s.[48,49,65] Gandini and coworkers, by using classic procedures, e.g. melt,[65] solution[49] and interfacial[49] polycondensations, have prepared linear regular polymeric structures with reasonably high molecular weights. Polycondensation in solution of 2,2'-bis(5-chloroformyl-2-furyl)propane (R=Cl and both R' and R''=CH_3 in Fig. 25) with a number of diols showed to be an interesting route to obtain furan polyesters identical to those prepared by melt polycondensation with similar molecular weights, whereas interfacial polycondensation revealed to be a viable way to produce difuran-aromatic structures with considerably higher molecular weights. This research also covered a detailed information on thermal transition temperatures and stabilility, as well as the relation between the variance of these parameters with both the nature of the R' and R'' groups of the difuran monomer and the structure of the diol. In particular, Tg values decreased from polyesters from aromatic diols to polyesters from aliphatic diols.

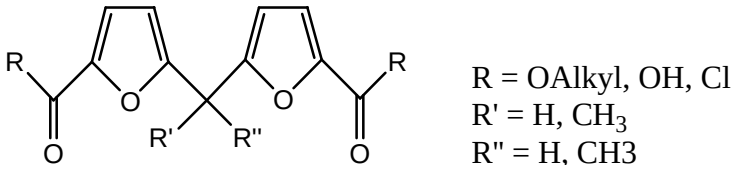


Fig. 25. General structure of the difuran-carboxylic derivatives.[48,49,65]

The first detailed research on the synthesis and characterization of polyesters derived from FDCA, which remained almost ignored after Moore's work, was carried out by Gandini *et al.*[20,21] in our laboratory in the course of the last few years. The first investigation dealt with a hitherto almost forgotten polymer, poly(ethylene 2,5-furandicarboxylate) (PEF) (Fig. 26, x=2), which is the heterocycle homolog of the most important commercial polyester, PET.[20,66]

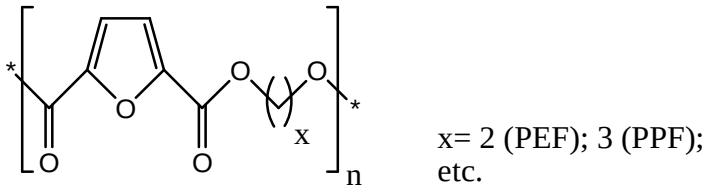


Fig. 26. General structure of furan-aliphatic polyesters.

The furan-aliphatic polyester, PEF was prepared by melt polycondensation of bis(hydroxyethyl)-2,5-furandicarboxylates, using Sb_2O_3 as catalyst in a high vacuum system under magnetic stirring, with the temperature increasing from 70 to 220 ºC. The ensuing polyesters were stable up to ~300 ºC, as suggested by thermogravimetric analysis (TGA), and displayed a thermal behaviour similar to that of PET. A high degree of crystallinity was suggested by differential scanning calorimetry (DSC), i.e. no glass transition detected and a melting transition at 210-215 ºC (~45 ºC lower than that of PET) during the heating of the precipitated PEF to 250 ºC. The high crystallinity of PEF was confirmed by its X-ray diffraction pattern. After quenching from the melt, the amorphous domains of PEF displayed a Tg at 75-80 ºC, and a crystallization exotherm at ~165 ºC, which confirms its high aptitude to crystallize. From the results of elemental analysis DPn values of 250-300 were reported for the polymer.[20,66]

The same authors also reported the synthesis of PEF using the solution polycondensation involving the FDCDCl and ethylene glycol, but, unfortunately, only structures with low DPn (of about 70) were obtained.[21,66]

The synthesis and characterization of poly(propylene 2,5-furandicarboxylate) (PPF) (Fig. 26, x=3), the furan version of PPT, were also reported.[21,67] As expected, both the Tg of 65 ºC and Tm of 174 ºC were lower than those of PEF, as a result of the additional macromolecular flexibility conferred by the additional methylene moiety in each polymer repeating unit. As for PEF, DPn values of ~250 were reported for PPF.

Identical furan-aliphatic polyesters to PEF and PPF were synthesized by combining FDCA dimethyl ester with 1,6-hexanediol, 1,12-dodecanediol and 1,18-octadecanediol (Fig. 26, x=6, 12, and 18 respectively).[68] High molecular weight polyesters were obtained (M_w over 30 000 g/mol). The thermal analysis by DSC suggested Tm values lower than that of PEF, which are in accordance with the flexible effect provided by the extension of the aliphatic chain. Tg values were only reported for PPF, and was lower than that previously reported by Gandini *et al*.[20,21,66]

Concluding, the results published so far prove the potential of furan derived polyesters, and open the possibility of proposing novel materials, alternative to those obtained from petrochemistry, based on FDCA and diols, which are already considered as future promising chemicals from renewable resources, e.g. EG and PDO.[5,9] The production of copolyesters and their thorough characterization will also be an interesting contribution to widen this family of macromolecular structures.

4. Objectives

Motivated by both the current predictions on the large-scale production of 2,5-furandicarboxylic acid (arising from the recent efforts on the efficient production of 5-hydroxymethylfurfural) and its well established potential as a precursor in polymer synthesis, this work aimed at contributing for its valorisation by developing novel polyesters from it.

As a result, the main objective falls into the synthesis of new polyesters from 2,5-furandicarboxylic acid by well-known polycondensation procedures using diverse diols of both natural and synthetic origin, and subsequent characterization of the ensuing materials in the light of a comparison with their petroleum-based homologs. More specifically:

- the synthesis and characterization of FDCA derived monomers, e.g. 2,5-furandicarbonyl dichloride and dimethyl 2,5-furandicarboxylate;
- the synthesis of polyesters by combining the aforementioned monomers with diols of diverse origins, e.g. 2,5-bis(hydroxymethyl)furan (other interesting HMF derivative), 1,4-cyclohexanedimethanol and 1,4-butanediol, using conventional polycondensation techniques;
- the detailed characterization of the ensuing materials in terms of both structural characteristics, thermal and mechanical properties.

5. Results and discussion

5.1. Preparation of starting monomers

This section describes the synthetic strategies as well as the characterization of the furan monomers used for preparing the proposed polyesters. The specificities associated with the different polymerization strategies as well as with the different polymers will be discussed in section 5.2.

2,5-Furandicarboxylic acid, was a generous gift from Prof. Claude Moreau of Ecole Nationale Supérieure de Chimie de Montpellier,[17] and was used as received, since its purity, as confirmed by ^{1}H and ^{13}C NMR spectroscopy, was found to be adequate for its use as a precursor of the furan monomers required for this study (see section 5.1.2.1).

The various commercial diols, viz. 2,5-bis(hydroxymethyl)furan (BHMD), cis/*trans*-1,4-cyclohexanedimethanol (CHDM, mixture of *cis* and *trans* isomers, 30/70 isomer ratio) and 1,4-butanediol (BDO) (Fig. 27), required to prepare the proposed furan-based polyesters were also characterized by ^{1}H and ^{13}C NMR spectroscopy, which just confirmed their structure and purity (see section 7.1.1).

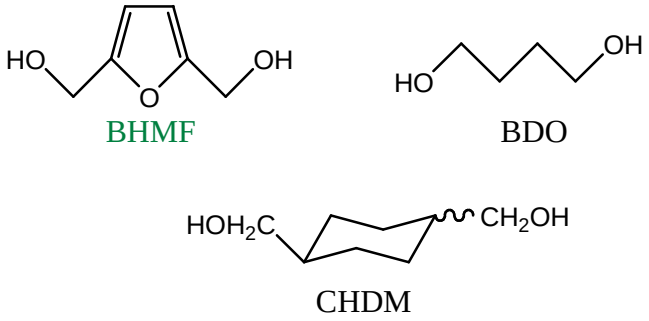


Fig. 27. Starting diol monomers used to prepare FDCA polyesters; green represents the diol used in the interfacial experiment; black represents those used in melt.

The two starting furan monomers required for this study were DMFDC and FDCDCl which arise from direct conversion of FDCA. Whereas the latter can be directly used as a monomer for polymer synthesis, the former can be used as a precursor of bis(hydroxyalkyl)-2,5-furancarboxylate type structures, which, as discussed before, will be the direct monomers for melt polycondensation itself, in a continuous process of prepolymerization and polymerization (see section 2.1.1.1 for details).

5.1.1. FDCA monomers synthesis

5.1.1.1. 2,5-Furandicarbonyl dichloride (FDCDCl)

The production of FDCDCl can be carried out as reported by Kelly[55] by using phosphorous pentachloride (PCl_5), in yields of 75%. However, this methodology requires the use of several solvents both to conduct the reaction and to isolate the diacid dichloride which appeared to be quite soluble in diethyl ether. Recently, a new route was adopted by Gandini *et al*.,[21,66] which, due to its feasibility, was used in this work.

The proposed method consists in the treatment of FDCA with an excess of $SOCl_2$ under reflux for 4h, in the presence of DMF as catalyst (Fig. 28). Given that $SOCl_2$ is already a liquid, no additional solvents are required. Initially, a heterogeneous mixture was observed, which just confirmed the insolubility of the diacid in $SOCl_2$. As the reaction proceeded, a homogeneous media was observed, confirming thus the formation of the FDCDCl, which at 80 ºC (FDCDCl melted at this temperature) appears completely mixed with the excess of $SOCl_2$. By cooling to room temperature, and after evaporation of the solvent and byproducts, the resulting solid was then purified by successive vacuum sublimations at 55 ºC to give white crystals (in the form of needles) which recrystallized in hexane, and were then collected by suction filtration. By concentring the filtrate to about half its volume and stored in the fridge, a second crop of FDCDCl could be isolated. This procedure was repeated till no more recrystallization was observed. The total yield was about 70%.

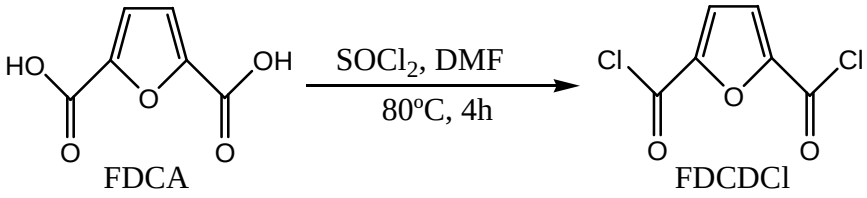


Fig. 28. FDCDCl synthesis.

5.1.1.2. Dimethyl 2,5-furandicarboxylate (DMFDC)

According to the procedure adopted by Gandini *et al*.,[21,66] which results from an update of that one firstly used by Haworth and Jones,[69] the dimethyl ester (DMFDC) was prepared by acid-catalysed Fisher esterification of FDCA with an excess of methanol in the presence of a mineral acid, e.g. HCl (Fig. 29).The reaction product, as white precipitate, was then isolated by filtration, and the filtrate neutralized by adding

concentrated NaOH. By washing a small fraction of the solid with acetone, it was allowed to separate two different fractions, namely a soluble fraction and an insoluble one, which were attributed to the DMFDC and monoester (Fig. 29) respectively, as suggested by FTIR and NMR analysis of the fractions. In this sense, the purification of the diester was carried out by consecutively washing the solid obtained from the reaction with acetone, followed by filtration, till no more diester was separated. The diester obtained from these filtration processes appeared to be highly pure, as suggested by NMR spectroscopy (see section 5.1.2.2). A total yield of ~50% was achieved. The monoester can latter be reutilized in the above mentioned Fischer esterification step.

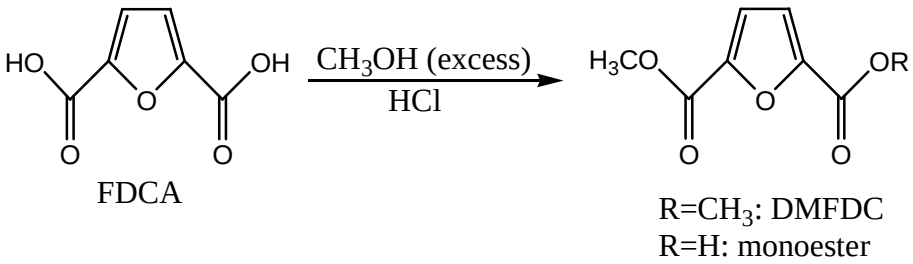


Fig. 29. General scheme of DMFDC synthesis.

5.1.2. Monomers characterization

5.1.2.1. 2,5-Furandicarboxylic acid

Given that FDCA is the most important reactant in the context of this work, its characterization, before entering to the characterization of the diverse FDCA derived monomers, should be considered. Therefore, the received FDCA was structurally characterized by FTIR and ^{1}H and ^{13}C NMR spectroscopy as described next.

The FTIR spectrum of FDCA (Fig. 30) displays the expected[66,67,70] stretching and bending absorption bands of the characteristic functional groups, especially that correspondent to the carbonyl group (C=O) stretching vibration, which occurs at 1675 cm^{-1}. In accordance to the literature, the absorption arising from C=O stretching in carboxylic acids occurs near 1760 cm^{-1}.[70] The decrease, found in this specific case, can be explained by conjugation effects of the carbonyl group with the unsaturations of the furan ring. Other characteristic band of carboxylic acids occurs in the 3000-2400 cm^{-1} region and is attributed to the very intensive O−H stretching absorption.

Still on the carboxylic group, two bands arising from C−O stretching and O−H bending appears at 1274 and 1418 cm^{-1}, respectively.

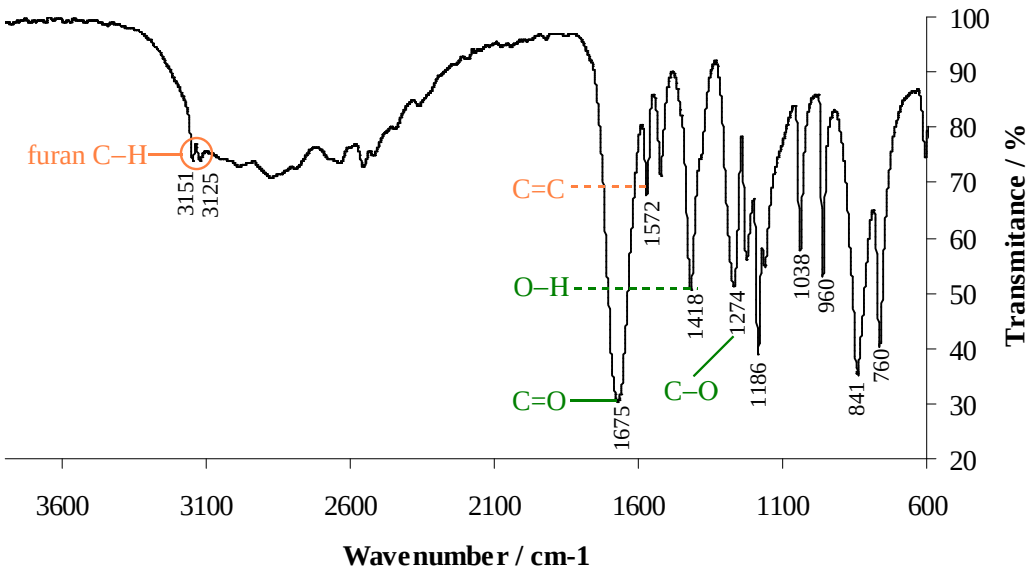


Fig. 30. FTIR spectrum of FDCA; green represents the characteristic bands of carboxylic acids; orange represents those for the furan ring.

The remaining relevant IR bands are typical vibrational excitations of the 2,5-disubtituted furan heterocycle, viz.: two bands at 3151 and 3125 cm^{-1} (somewhat obscured due to the carboxylic acid O−H stretch cloud) arising from the C−H stretching vibration at C-3,4 positions, another one occurring at 1572 cm^{-1} that results from the C=C stretching absorption, the characteristic band of heterocycle breathing at 1038 cm^{-1}, and finally the characteristic bands related to the bending motions associated with the 2,5-disubstituted furan occurring at 960, 841, and 760 cm^{-1}. These attributions were made by comparing with similar structures reported in the literature.[20,21,66,67,70,71]

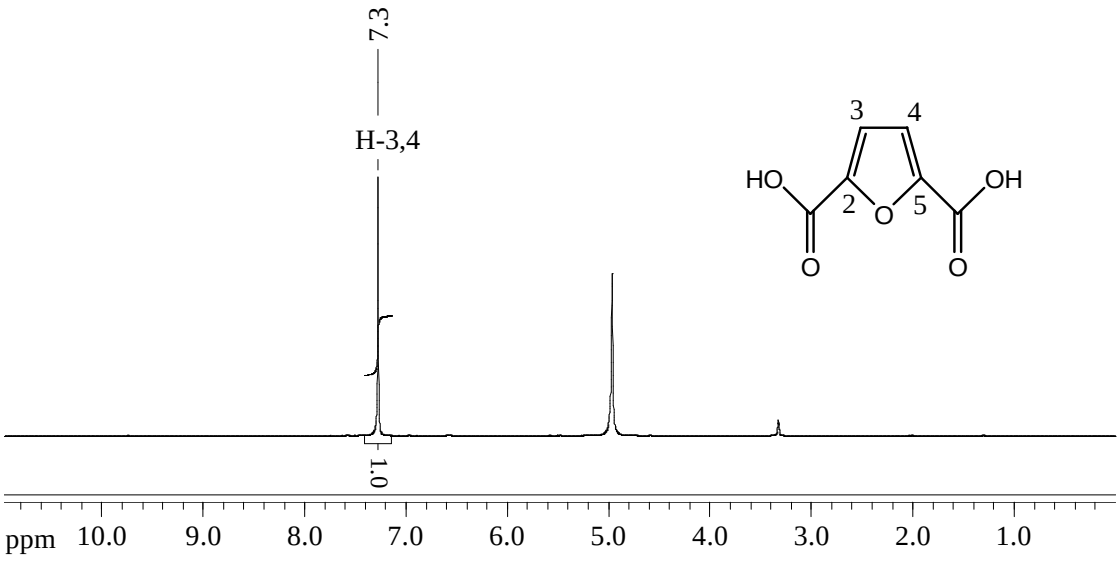


Fig. 31. Typical ^{1}H NMR spectrum of FDCA in CD_3OD solution (ppm from TMS).

The ^{1}H and ^{13}C NMR spectra obtained for FDCA allow us to confirm the proposed structure from FTIR spectrum. The ^{1}H NMR spectrum (Fig. 31) exhibits a unique peak as a singlet at 7.3 ppm, which is attributed to the resonances of H-3,4 protons of the furan heterocycle.[20,21,66,67,70,71] No resonances of protons involved in hydrogen bonds, i.e. attributed to the carboxylic group, are detectable for chemical shifts higher than 10 ppm, where they would be expected to occur.[72]

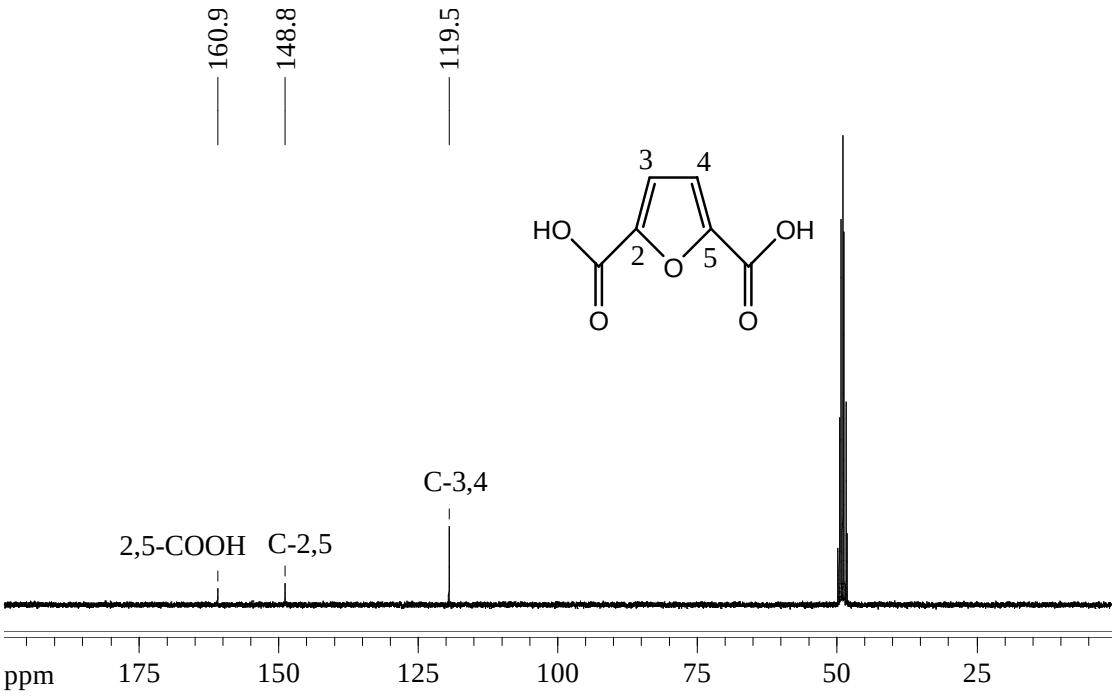


Fig. 32. Typical ^{13}C NMR spectrum of FDCA in CD_3OD solution (ppm from TMS).

The ^{13}C NMR spectrum of FDCA (Fig. 32) shows the presence of several resonances, assigned using the literature as support.[20,21,66,67,70] Thus, it was found that:

- the peak at 160.9 ppm corresponds to the resonances of 2,5-CO carbonyl carbons, since this chemical shift is in the characteristic chemical shift region of resonances of carbonyl carbons of carboxylic groups (150-185 ppm);
- the peak at 148.8 ppm corresponds to the resonances of C-2,5 carbons, since this chemical shift is characteristic of resonances of these carbons in 2,5-disubstituted furan rings;
- the peak at 119.5 ppm corresponds to the resonances of C-3,4 carbons of the furan heterocycle.

5.1.2.2. FDCA derived monomers characterization

Just as for FDCA, all the monomers structures were inspected and confirmed by FTIR and ^{1}H and ^{13}C NMR spectroscopy. Due to structural and spectroscopic features common to all monomers, their discussion is drawn together.

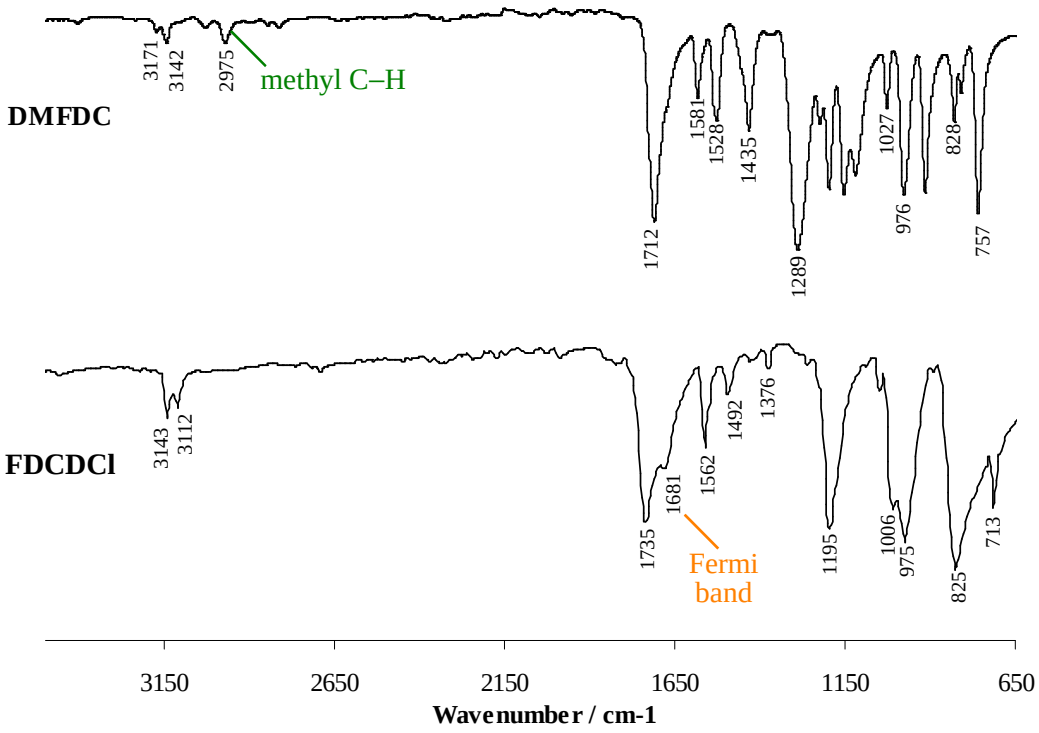


Fig. 33. FTIR spectra of DMFDC and FDCDCl.

The typical FTIR spectra of FDCDCl and DMFDC are shown in Fig. 33 and, as discussed bellow, were consonant with the expected structures. Table 2 gives the frequencies and assignments of the typical bands of FDCA, FDCDCl and DMFDC.

By comparing the results obtained for FDCDCl and DMFDC with those obtained for FDCA, it was found that, apart from the characteristic bands of the 2,5-disubstituted furan, viz. the C=C stretch absorption, ring breathing, and out-of-plane =C−H deformations, some bands of the FTIR spectrum of FDCA have disappeared or displaced, leading to the occurrence of some new bands in both spectra, viz.:

- the disappearance of the band corresponding to the O−H stretch absorption of FDCA at 3000 – 2357 cm^{-1} region in both cases, due to the functionalization of the COOH groups (with Cl or CH_3), with an improvement on the definition of those bands arising from furan =C−H stretch vibrations;

- the displacement of the typical band of carbonyl group of carboxylic acids to higher wavenumbers, viz. from 1675 to 1712 and 1732, respectively, due to the conversion of FDCA into its dimethyl ester and dichloride, respectively;
- the appearance of a new band at 2975 cm^{-1} in the spectrum of DMFDC, which is attributed to the presence of methyl groups in the molecule;
- the appearance of a shoulder-type band at 1681 cm^{-1} in the spectrum of FDCDCl, which is known as the ''Fermi resonance band''[70] (of C=O stretch and overtone of 884 cm^{-1} band), a typical band of acyl chlorides.

Table 2. Assignment of the FTIR bands relative to FDCA, FDCDCl, and DMFDC.

FTIR - ATR	**FDCA**	**FDCDCl**	**DMFDC**
	ν (cm^{-1})		
Furan =C–H stretch	3151, 3125	3140, 3110	3171, 3142
O–H stretch	3000 - 2357	–	–
C–H (methyl) stretch	–	–	2975
C=O stretch	1675	1737	1712
Furan C=C stretch	1572	1563	1525
C–O–H bend	1418	–	–
C–O stretch	1274	–	1292
Ring breathing	1038	1007	1027
2,5 - disubstituted ring (bending motions)	960, 841, 760	974, 824, 712	976, 828, 757

The ^{1}H NMR resonances of FDCA and its two derivatives (FDCDCl and DMFDC) are listed in Table 3. The corresponding assignments were made with the aid of the literature in spectroscopic characterization of similar structures.[20,21,66,67,70]

Table 3. Assignment of the ^{1}H NMR chemical shifts relative to FDCA, FDCDCl, and DMFDC; multiplicity (m); number of protons (nH).

^{1}H NMR	**FDCA** (CD_3OD)	**FDCDCl** ($CDCl_3$)	**DMFDC** ($CDCl_3$)
	δ (ppm); m; nH		
H-3,4	7.2; s; 2H	7.5; s; 2H	7.2; s; 2H
$C\underline{H}_3$	–	–	3.9; s; 6H

When compared with FDCA, these two monomers shared the same resonance characteristic of H-3,4 protons of the furan heterocycle, at 7.2 and 7.5 ppm, respectively for DMFDC and FDCDCl, in the form of singlet peaks. This variation in chemical shifts arises from the effect of the substituent groups at C-2,5. In this sense, the highest chemical shift, viz. 7.5 ppm, induced by the resonances of H-3,4 protons of FDCDCl, is explained by their higher deprotection, a result from the higher electronegativity of the chloride group attached to the carbonyl carbon. Additionally, the ^{1}H NMR spectrum of DMFDC (Fig. 34) evidences a singlet peak at 3.9 ppm, which is attributed to the resonances of protons of the methyl group (2,5-$COOCH_3$).

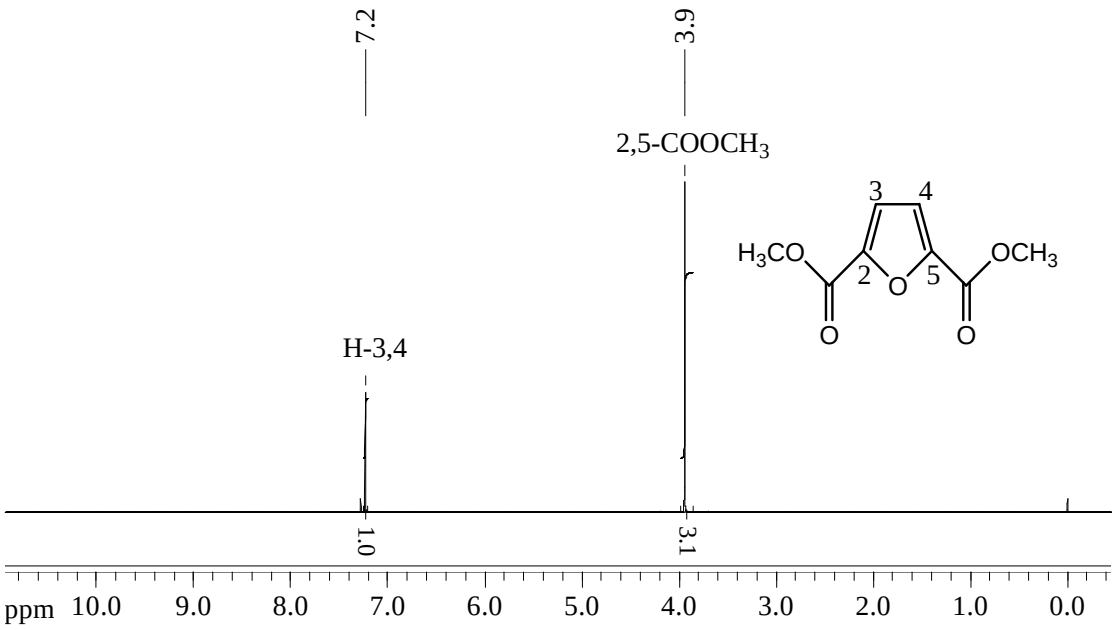


Fig. 34. Typical ^{1}H NMR spectrum of DMFDC recorded in CD_3OD (ppm from TMS).

From the ^{13}C NMR spectra of FDCDCl and DMFDC, whose data are summarized in Table 4, it was found that the resonances of the carbonyl carbon occur at 158.4 and 155.9 ppm, respectively for DMFDC and FDCDCl, as expected for carboxylic acids and derivatives attached to the furan ring and the effects induced by the presence of Cl or OCH_3 groups.[70] The resonances of the carbons of the furan ring occur at 146.6 and 149.3 ppm for C-2,5 and at 118.4 and 123.2 ppm for C-3,4 carbons in DMFDC and FDCDCl respectively. These assignments were in accordance with those established for carbons present in 2,5-disubstituted furan.[20,21,66,67,70]

Table 4. Assignment of the ^{13}C NMR chemical shifts relative to FDCA, FDCDCl, and DMFDC.

^{13}C NMR	**FDCA** (CD_3OD)	**FDCDCl** ($CDCl_3$)	**DMFDC** ($CDCl_3$)
	δ (ppm)		
C-2,5	148.8	149.3	146.6
C-3,4	119.5	123.2	118.4
2,5-C=O	160.9	155.9	158.4
2,5-COO<u>C</u>H_3	–	–	52.4

The ^{13}C NMR spectrum of DMFDC (Fig. 35) also evidences the occurrence of a peak at 52.4 ppm, which is attributed to the resonance of the methyl carbon (2,5-COO<u>C</u>H_3).

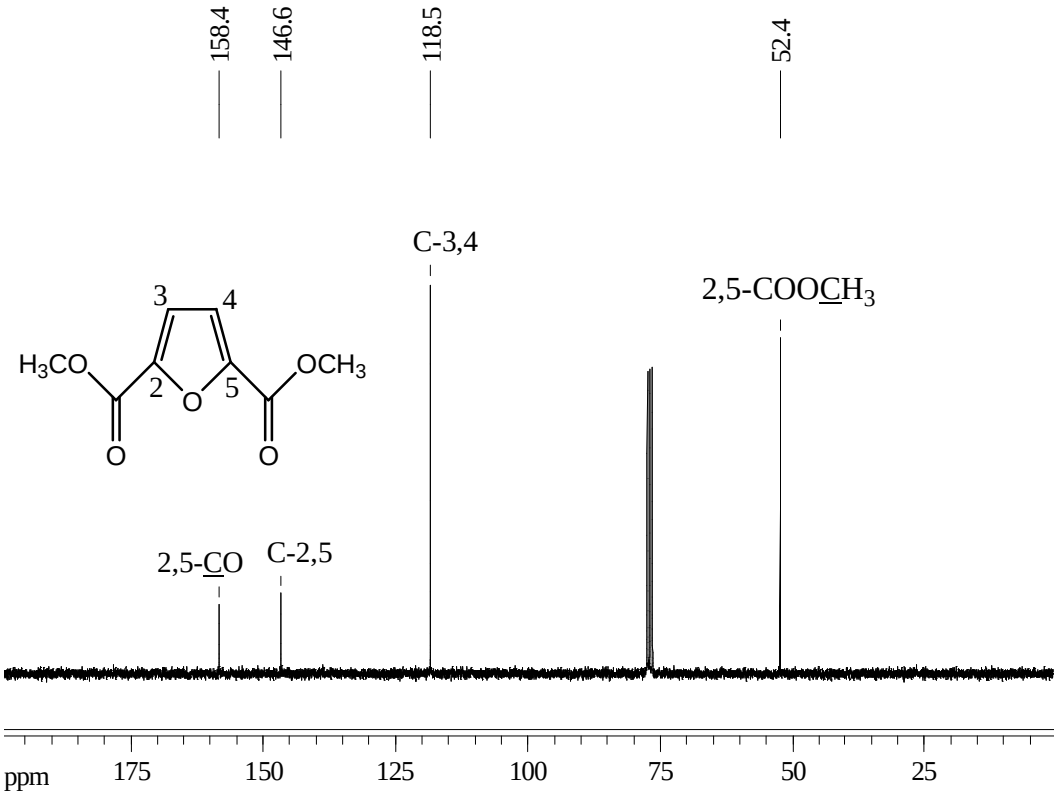


Fig. 35. Typical ^{13}C NMR spectrum of DMFDC in $CDCl_3$ solution (ppm from TMS).

The characterization of the different monomers also included their thermal characterization by measuring the melting temperatures (Tm) through DSC. These values are given in Table 5.

Table 5. Melting temperatures of the diverse monomers.

DSC	FDCA	FDCDCl	DMFDC
	ºC		
Tm	334	79	110

When compared with its derivatives, FDCA has a much higher value of Tm, 334 ºC, which can be a result of its strong cohesive energy associated with both the occurrence of intermolecular hydrogen bonds and its crystalline organization. Since FDCDCl and DMFDC do not exhibit these interactions, they have lower Tm values.

5.2. Polymers preparation

The polymers prepared in this study are linear polyesters, so that they were synthesised by conventional methods of polycondensation. Particularly, melt and interfacial polycondensations were used with respect to the proposed diols discussed in section 5.1. Thus, two different classes of polyesters were prepared, namely furan-furan and furan-aliphatic polyesters, with the former comprising the polymer resulting from the combination of FDCDCl with BHMF by interfacial polycondensation, viz. Poly(2,5-furandimethylene 2,5-furandicarboxylate) (PFDMF), whereas the latter comprises two polymers arising from the combination of DMFDC with CHDM and BDO by melt polycondensation, viz. poly(1,4-cyclohexylenedimethylene 2,5-furandicarboxylate) (PCHDF) and poly(butylene 2,5-furandicarboxylate) (PBF), respectively. After synthesis and purification, all polymers were characterized in detail as discussed in section 5.2.2.

5.2.1. Polymers synthesis

5.2.1.1. Poly(2,5-furandimethylene 2,5-furandicarboxylate) (PFDMF)

The synthesis of PFDMF was firstly carried out by Moore and Kelly,[55,56] by solution polycondensation using chloroform as solvent. However, the formed polymer was found to precipitate during the polymerization. Since aromatic diols are well suited for interfacial polycondensation, this method was adopted in this work, following similar conditions to those reported by Gandini *et al.*[21,66] for the synthesis of furan-aromatic polyesters based on FDCA.

Thus, its synthesis was carried out by interfacial polycondensation using an alkaline NaOH aqueous solution/organic phase (DCM) system vigorously stirred at room temperature, and with tetra-n-butyl ammonium bromide (TBAB) as phase-transfer agent (Fig. 36). Equal molar amounts of the diol and diacid dichloride were dissolved in the basic aqueous solution and organic solvent, respectively, to give a 0.1 M concentration of diacid dichloride in the organic phase and a 0.05 M concentration of the diol in the aqueous phase. Solid particles immediately surged at the interface suggesting the occurrence of polymerization. When there was no more precipitation the reaction was stopped. The aqueous solution was then neutralized and the polymer isolated by successively filtrating and washing with methanol. By using this system of isolation, it was found that the small-chain oligomers were solubilised in methanol whereas the high-molecular-weight chains of polymer did not, as suggested by FTIR and NMR analysis of the two fractions.

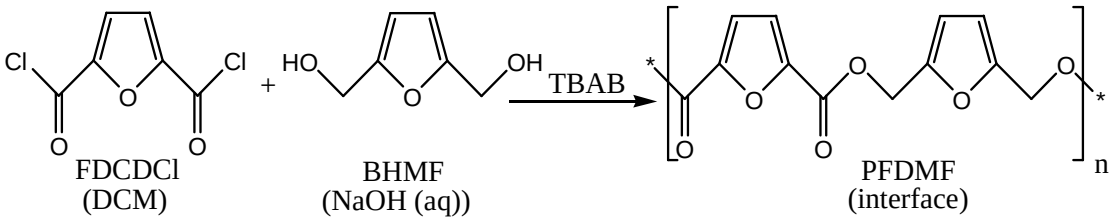


Fig. 36. Illustrative scheme of PFDMF synthesis.

As a mean of purification, the isolated PFDMFs were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and subsequently precipitated *via* dropwise addition of the HFP solution in an excess of methanol under stirring, followed by filtration, washing with methanol, and drying to constant weight, resulting in a light brown crystalline solid, ~60% yield.

The isolated and purified polymer was insoluble in TCE, $CHCl_3$, DCM, and only dissolved in trifluoroacetic acid (TFA) and HFP.

5.2.1.2. Poly(1,4-cyclohexylenedimethylene 2,5-furandicarboxylate) (PCHDF)

The synthesis of polyesters from CHDM has been carried out by the classical two-step melt polycondensation method,[73,74] as established for aliphatic diols. Thus, PCHDF was synthesised by combining a 1.5:1 excess of the mentioned diol with DMFDC and using zinc acetate ($Zn(OAc)_2$) as catalyst as illustrated in Fig. 37; the excess of diol may force the transesterification reaction/1st step towards completion and

compensate possible losses of the diol during all the experiment.[74] The tube containing the monomers and catalyst was rapidly heated to 100-110 ºC, under a nitrogen atmosphere. At this temperature, the melted DMFDC (m.p. ~110 ºC) forms a homogeneous solution with the excess of diol. The temperature was then increased to 180 ºC during the course of ~2.5 h under stirring, and the extension of the reaction of formation of the corresponding oligoesters was reflected by increases in the medium viscosity. Nearing 180 ºC, the viscosity has significantly increased, which, together with the condensation of the released methanol in the liquid nitrogen trap, suggested that oligomeric bis(hydroxyalkyl)esters were being formed. The system was then evacuated to ~10^{-3} bar and the temperature was progressively increased to 220 ºC in steps of 10 ºC, which ensured the immediate removal of the remaining methanol and sublimation of the excess of diol (confirmed by the surge of a white powder-type condensate in the trap column), allowing thus the reaction to proceed towards the production of high-molecular-weight polymers. After this point, it was possible to verify a significant increase in viscosity, suggesting therefore the occurrence of polymerization. At ~210 ºC, the highly viscous product turned into a solid mass, at which point the reaction was stopped by allowing the system to cool to room temperature.

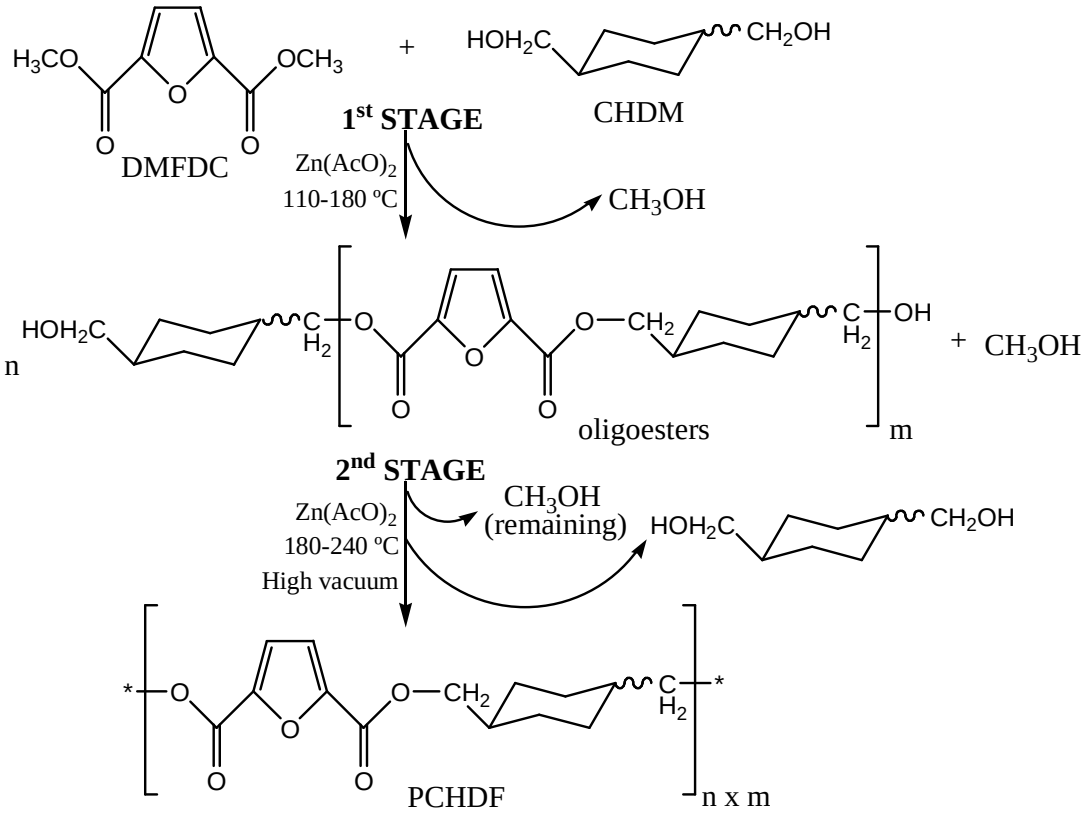
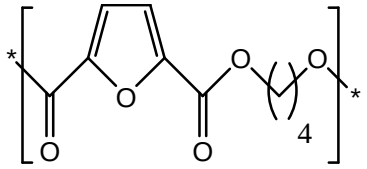


Fig. 37. General scheme of PCHDF synthesis by melt polycondensation.

Even though the polymer could be characterized as obtained, since no solvent was used for its synthesis and the amount of catalyst was very small, the product was purified, as described for PFDMF, in order to separate long chain polymers from small chain oligomers that eventually have not reacted. A light brown solid was obtained, ~65% yield, which, as PFDMF, only dissolved in TFA and HFP.

5.2.1.3. Poly(butylene 2,5-furandicarboxylate) (PBF)

The procedure adopted for the synthesis of the aforementioned furan-aliphatic polymer was generally followed to prepare PBF (Fig. 38), except that the diol as BDO. Unlike the former case, the temperature of ending of the 1st stage was ~160 ºC, which was established by the significant increase in the medium viscosity. After evacuating the system to ~10^{-3} bar and progressively increasing the temperature to 210 ºC, a highly viscous liquid was formed, which, unlike PCHDF did not solidify at 210 ºC.



PBF

Fig. 38. Structure of PBF.

After isolation and purification (as described for PCHDF), a light brown solid was obtained, ~55% yield, which was soluble in all solvents tested.

5.2.2. Polymers characterization

The polymers prepared as described above were characterized by FTIR and ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, TGA, DSC and X-ray diffraction.

5.2.2.1. Structural characterization

5.2.2.1.1. Poly(2,5-furandimethylene 2,5-furandicarboxylate)

The typical FTIR spectrum of PFDMF (Fig. 39) shows the bands associated with the 2,5-disubstituted furan heterocycle (=C−H and C=C stretches at 3129 and 1580 cm^{-1}, heterocycle breathing at 1024 cm^{-1}, and bending motions at 960, 798 and 764 cm^{-1}), and the ester carbonyl (C=O) and C−O moieties at 1716 and 1267 cm^{-1} respectively, and the characteristic band of aliphatic C−H stretching at 2973 cm^{-1} (i.e. C−H of

oxymethylene group (2,5−COO$\underline{CH_2}$) in this case).[20,21,66,67,70] When compared with FDCDCl (see Fig. 33), the typical band of carbonyl group is displaced to a lower wavenumber, 1716 cm^{-1} (characteristic of ester carbonyls), which just confirms the formation of ester linkages. Moreover, there is no evidence of any OH absorption band around 3400 cm^{-1}, and thus, considering that each polymeric chain has two terminal OH groups, this may suggest that PFDMFs had reached a reasonably high molecular weight.

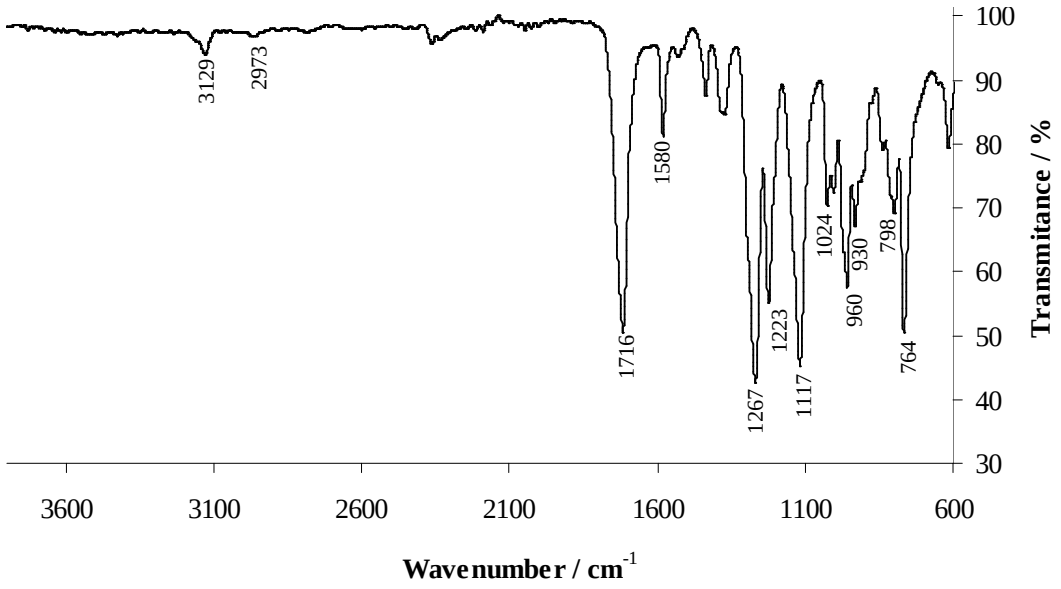


Fig. 39. Typical FTIR spectrum of PFDMF.

The characteristic ^{1}H and ^{13}C NMR resonances of PFDMF and the corresponding assignments are listed in Table 6. All the assignments were in accordance with those established for similar 2,5-disubstituted furan polyesters. [20,21,55,56,66,67]

Table 6. Assignment of the ^{1}H and ^{13}C NMR chemical shifts of PFDMF; multiplicity (m); number of protons (nH).

PFDMF	**^{1}H**	**^{13}C**
C_3F_6DOD	δ (ppm); m; nH	δ (ppm); m; nH
2,5	-	149.9
3,4	7.3; s; 2H	120.6
2,5-CO	-	160.6
2,5-$COOCH_2$	5.3; s; 4H	60.2
2',5'	-	147.1
3',4'	6.5; s; 2H	113.4

Its typical ^{1}H NMR spectrum (Fig. 40) is characterized by the presence of three peaks as singlets at 7.3, 6.5 and 5.3 ppm, which are attributed to the resonances of H-3,4, H-3',4', and 2,5-COOCH$_2$ protons, respectively. The higher chemical shift for the resonances of H-3,4 when compared with that one for H-3',4' is associated with the deshielding effect of the 2,5-dicarbonyl groups on these protons.

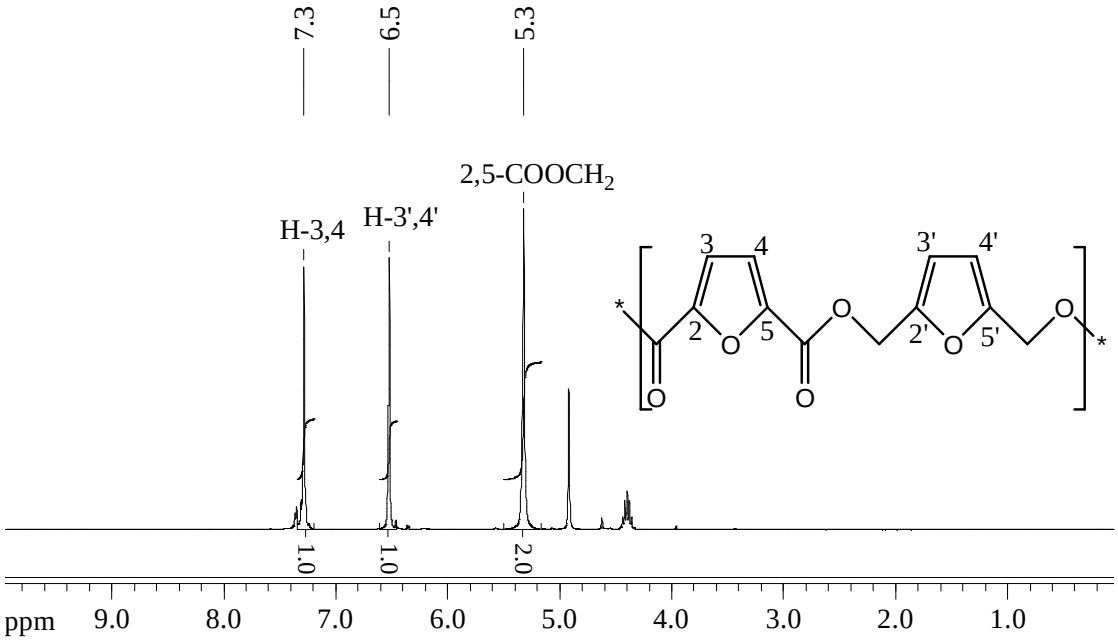


Fig. 40. Typical ^{1}H NMR spectrum of PFDMF recorded in C_3F_6DOD (ppm from TMS).

The ^{13}C NMR PFDMF spectrum is characterized by the presence of six resonance peaks, among which those associated with the furan carbons C-2,5, C-3,4, C-2',5' and C-3',4', at 149.9, 120.6, 147.1 and 113.4 ppm, respectively. The two peaks occurring at 160.6 and 60.2 ppm correspond to the resonances of the carbonyl carbon 2,5-CO and oxymethylenic carbon 2,5-COO<u>C</u>H$_2$ respectively. The higher chemical shifts for the resonances of C-2,5 and C-3,4 when compared with those for C-2',5' and C-3',4' carbons are associated with the effects of the 2,5-dicarbonyl groups on these carbons.

5.2.2.1.2. Poly(1,4-cyclohexylenedimethylene 2,5-furandicarboxylate)

The typical FTIR spectrum of PCHDF (Fig. 41) shows the characteristic bands of the 2,5-disubstituted furan heterocycle (3149 and 3113, 1577, 1018, 976, 827 and 764 cm^{-1}), and the bands corresponding to the ester carbonyl and C−O moieties at 1718 and 1270 cm^{-1} respectively, as well as the characteristic aliphatic C−H stretching

absorptions at 2923 and 2855 cm^{-1} (including both the oxymethylene and cycloaliphatic methylene and methine C−H stretching absorptions).[74,75] As for PFDMF, there is no evidence of any OH absorption band around its specific region, which may suggest that high molecular weight PCHDFs were formed.

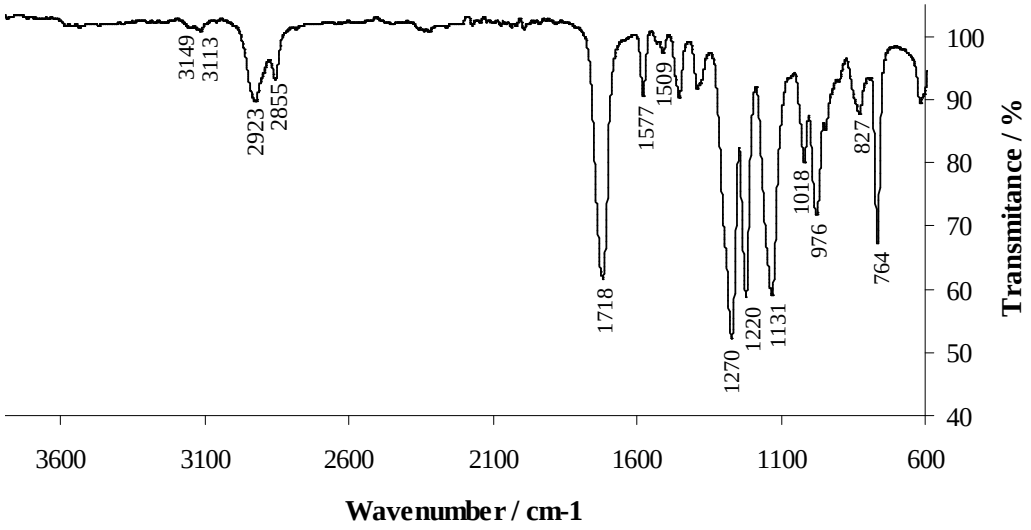


Fig. 41. Typical FTIR spectrum of PCHDF.

Fig. 42 shows the ^{1}H NMR spectrum of PCHDF. The singlet-type peak at 7.3 ppm corresponds to the resonances of the furan heterocycle protons H-3,4. The corresponding resonances of methylene protons of the oxymethylene groups (2,5-$COOCH_2$) as well as those of methylene and methine protons (H-6 and H-7, respectively) of the cyclohexane ring were assigned by comparing with similar structures based on *trans*- and *cis/trans* (35/65 mol% ratio)-1,4-cyclohexanedimethanols reported in the literature,[75,76] and by assuming that all 1,4-cyclohexylenedimethylene moieties are in their most stable conformation, namely the chain conformation.[77] Thus, it was found that the resonance peaks at 4.2 and 4.1 ppm correspond to the 2,5-$COOC\underline{H}_2$ methylene protons in the *cis*- and *trans*-isomers, respectively. The multiplets observed in the 1.4-1.9 ppm region and the peak at 1.0 ppm are associated with different environments of equatorial (eq) and axial (ax) H-6 and H-7 protons in *trans*- and *cis*-isomers. Except the two multiplets at 1.4 and 1.5 ppm, the remaining peaks represent typical resonances of *trans*-1,4-cyclohexanedimethanol based polyesters,[76] so that the formers are attributed to the resonances of eq and ax H-6 and H-7 protons in the *cis*-isomer. The resonance at 1.0 ppm and those in the region of 1.6-1.9 ppm represent ax H-6 protons and eq H-6 and ax H-7 protons, respectively, in the *trans*-isomer.

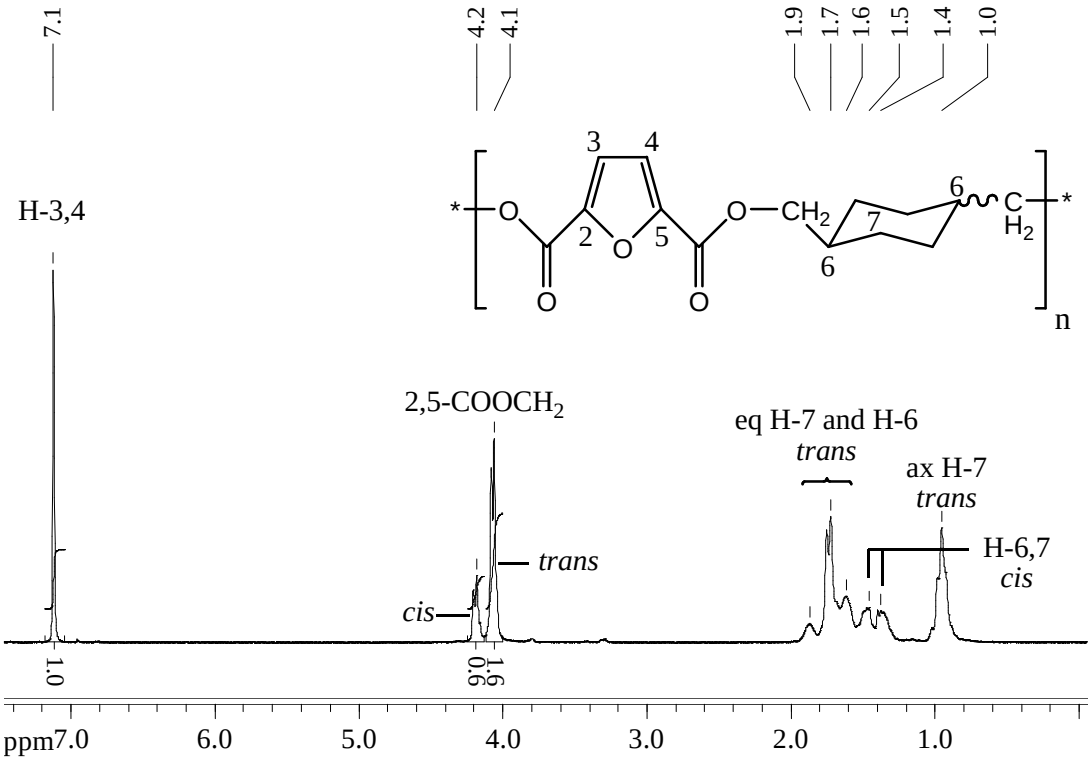


Fig. 42. ^{1}H NMR spectrum of PCHDF recorded in CF_3COOD (ppm from TMS).

The ^{13}C NMR spectrum of PCHDF is characterized by the presence of several resonance peaks, among which those attributed to the furan carbons C-2,5 and C-3,4 at 146.9 and 119.8 ppm, respectively, and carbonyl carbons at 161.4 ppm. The two peaks at 70.2 and 72.3 ppm represent the oxymethylenic carbons (2,5-COO$\underline{C}H_2$) in the *cis*- and *trans*-isomers, respectively. The resonances at lower chemical shifts, 24.7 and 28.2, and 34.5 and 37.0 ppm, represent methylenic and methinic carbons (C-6 and C-7) of the cyclohexane ring in the *cis*- and *trans*-isomers, respectively.

5.2.2.1.3. Poly(butylene 2,5-furandicarboxylate)

As for the previous polyesters, the typical spectrum of PBF (Fig. 43) shows the characteristic bands of 2,5-disubstituted furan heterocycle (3154 and 3120, 1576, 1032, 967, 862 and 766 cm^{-1}), and the bands corresponding to the ester carbonyl and C−O moieties at 1716 and 1271 cm^{-1} respectively. The main chain methylene C−H absorbs at 2965 and 2897 cm^{-1}, as expected for these groups. As for the above polyesters, there is no evidence of any OH absorption band around its specific region, which may suggest that PBFs had reached a reasonably high molecular weight.

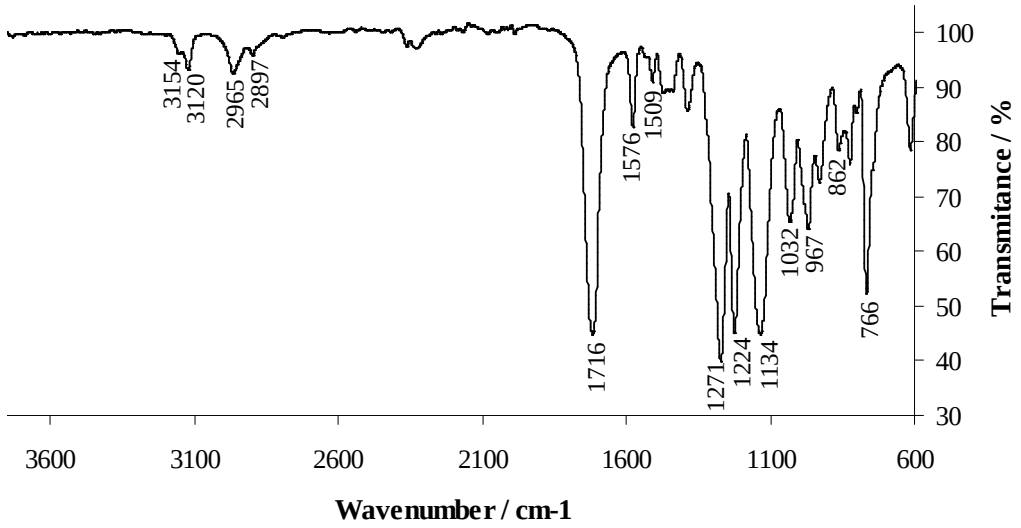


Fig. 43. Typical FTIR spectrum of PBF.

The data related to the ^{1}H and ^{13}C NMR spectra of PFDMF are listed in Table 7. All the assignments were in made accordance with those established for similar 2,5-disubstituted furan polyesters.[20,21,66,67,72]

Table 7. Assignment of the ^{1}H and ^{13}C NMR chemical shifts of PBF; multiplicity (m); number of protons (nH).

PBF	**^{1}H**	**^{13}C**
CD_3OD	δ (ppm); m; nH	δ (ppm); m; nH
2,5	-	147.6
3,4	7.2; s; 2H	118.5
2,5-CO	-	157.9
2,5-$COOCH_2$	4.4; s; 4H	64.9
2,5-$COOCH_2CH_2$	1.9; s; 4H	25.2

Its ^{1}H NMR spectrum (Fig. 44) is characterized by the presence of three peaks as singlets at 7.2, 4.4 and 1.9 ppm, which are attributed to the resonances of H-3,4, 2,5-$COOCH_2$, and 2,5-$COOCH_2C\underline{H}_2$ protons, respectively. The unexpected additional peak at 3.9 ppm, may be associated with $-COOCH_2CH_2CH_2CH_2OCH_2CH_2CH_2CH_2OOC-$ ether groups formation, as previously reported for its PEF homolog.[66] In this sense, this resonance peak is attributed to the corresponding $C\underline{H}_2OC\underline{H}_2$ methylene protons.

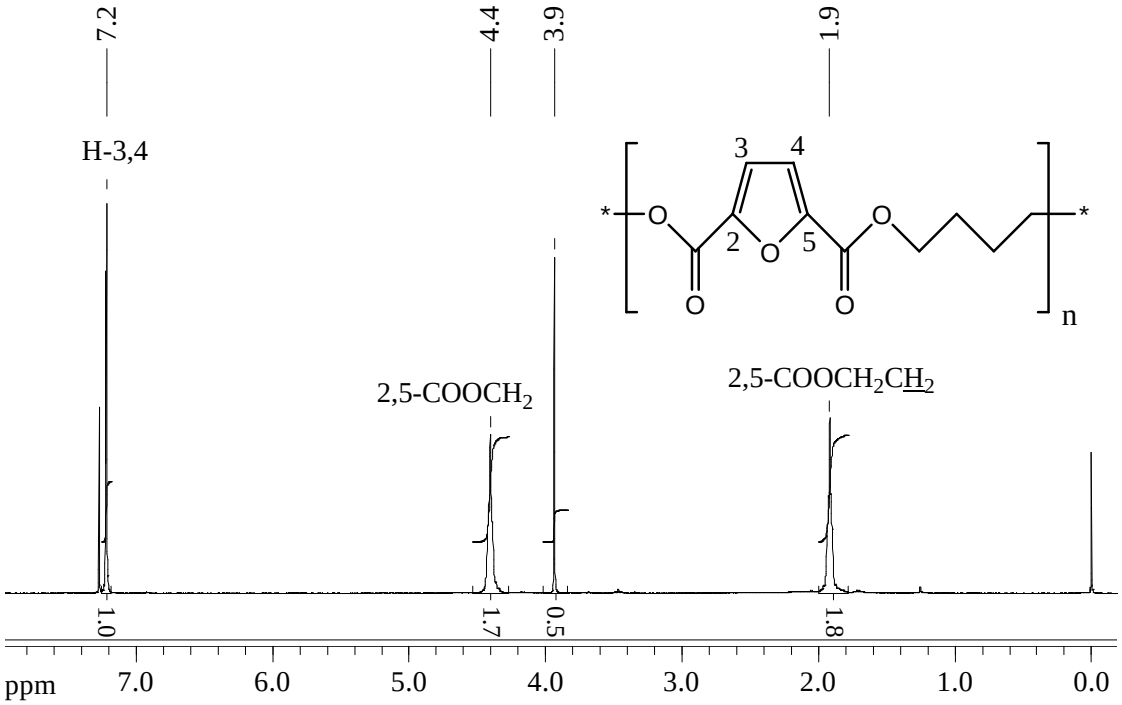


Fig. 44. ^{1}H NMR spectrum of PBF recorded in CD_3OD (ppm from TMS).

Its ^{13}C NMR spectrum is characterized by the presence of five peaks, among which those attributed to the resonances of furan carbons C-2,5 and C-3,4 at 146.7 and 118.5 ppm respectively, and carbonyl carbons at 157.9 ppm. The two peaks at 64.9 and 25.2 ppm are attributed to the resonances of the main chain 2,5-COO$\underline{C}H_2$ and 2,5-COOCH$_2\underline{C}H_2$ methylenic carbons, respectively. The resonance peak corresponding to the presupposed $\underline{C}H_2O\underline{C}H_2$ methylenic carbons surges at 52.4 ppm (Fig. 45).

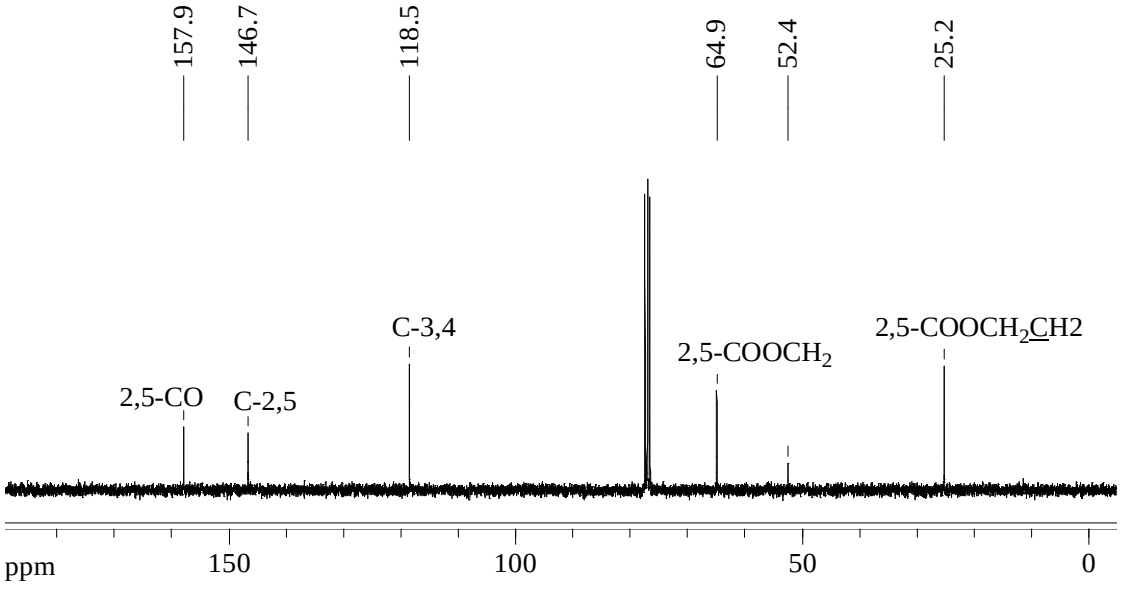


Fig. 45. ^{13}C NMR spectrum of PBF recorded in CD_3OD (ppm from TMS)

5.2.2.2. Elemental analysis

The elemental composition of all polyesters was determined by the elemental analysis of carbon (%C) and hydrogen (%H), considering the content of oxygen (%O) as the difference to 100 % of the sum %C + %H (%O = 100 – (%C + %H)). These values were then compared with those calculated for the repeating units of each polymer, and are listed in Table 8.

Table 8. Elemental analysis of PFDMF, PCHDF and PBF.

Element		Calculated values	Obtained values
PFDMF	%C	58.07	55.26
	%H	3.25	3.77
	%O[a]	38.68	40.97
PCHDF	%C	63.63	63.25
	%H	6.10	7.45
	%O[a]	30.27	29.30
PBF	%C	57.14	–
	%H	4.80	–
	%O[a]	38.06	–

[a] %O = 100 - %C - %H.

The results obtained for PFDMF, when compared with those calculated for their repeating units, show a slight decrease in %C and an increase in %H and %O, which may suggest the presence of residual H_2O in the sample. The possibility of existence of low molecular weight oligomers is excluded, since it contradicts what was previously suggested by FTIR and ^{1}H and ^{13}C spectroscopy.

The results obtained for PCHDF, were found to be more concordant with those calculated for the repeating unit.

5.2.2.3. Thermal analysis

The thermal stability of the polyesters was characterized by means of TGA. The temperature of the onset of degradation (3% weight loss temperature, Ti) and the maximum decomposition temperature (Tmax), relative to all polymers, are listed in Table 9.

Table 9. Temperatures of decomposition, Ti and Tmax, relative to all polyesters.

TGA	PBF	PCHDF	PFDMF
Ti (ºC)	347	340	205
Tmax (ºC)	402	412	345

PBF was found to be thermally stable up to ~330 ºC and degraded thereafter in a unique decomposition step (Fig. 46), which led to almost its complete decomposition at 402 ºC (Tmax), remaining only a ~5% residue, which was found to resist till 800 ºC. This behaviour is similar to that displayed by its petrobased counterpart, PBT, albeit with a ~30 ºC lower Ti.[78] When compared with its PEF and PTF homologs, PBF possesses the highest thermal stability.[20,21,66,67]

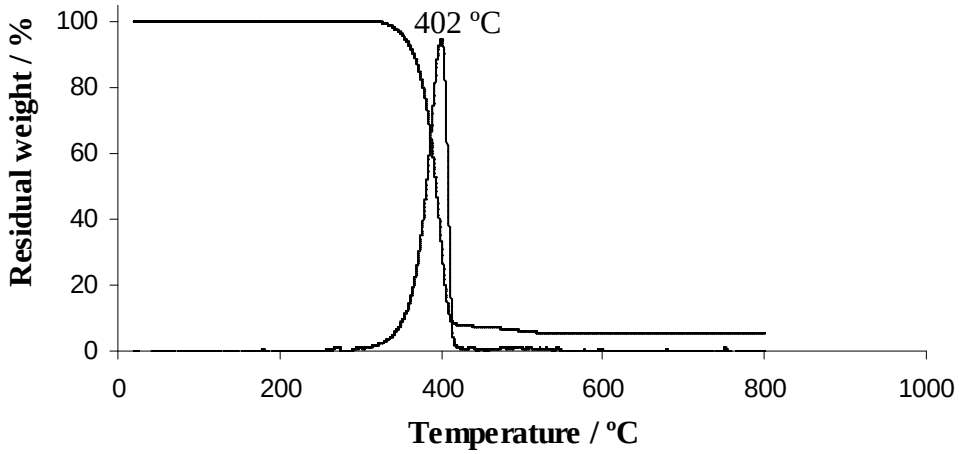


Fig. 46. Typical TGA thermogram of PBT in a nitrogen flow.

A similar behaviour to that of PBF was presented by PCHDF. According to the results obtained for both polymers, they were found to have substantially the same thermal stability (see Table 9).

The fully furanic polyester, PFDMF, presented a different behaviour from that displayed by the above polyesters, and started decomposing to a black insoluble material at ~180 ºC. This disappointing behaviour was also reported by Kelly and Moore,[55] and it was proved in this work to lead to the formation of low molecular weight structures bearing both carboxylic acid and methylene groups, as suggested by the FTIR spectrum (Fig. 47) of the white product sublimated at 180 ºC and under high vacuum. This phenomenon goes in accordance with the established instability of the hydrogen atoms in the methylene groups attached to furan ring.[18,19]

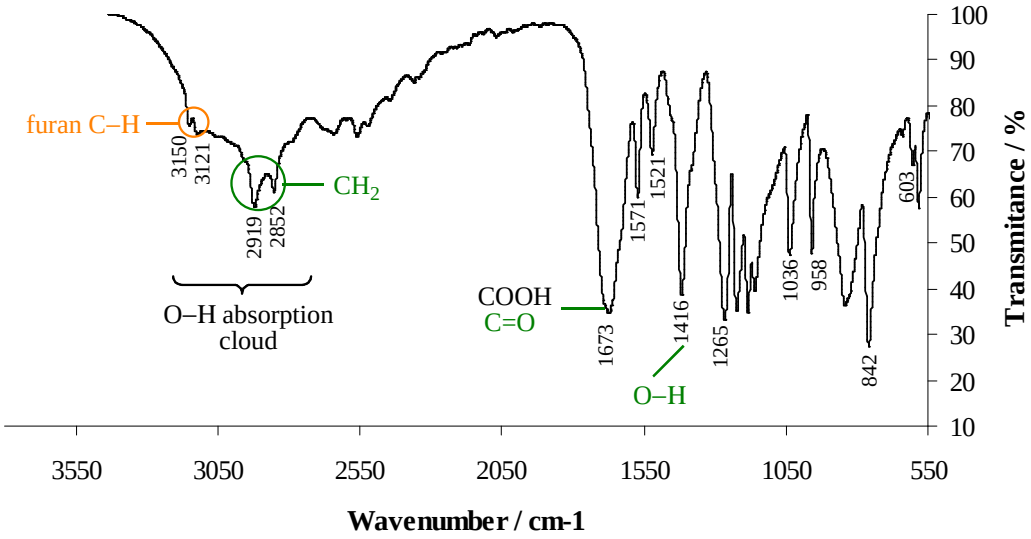


Fig. 47. FTIR spectrum of the product of decomposition of PFDMF after sublimation.

The thermal transitions relative to all polymers were determined from DSC measurements before and after quenching them from the melt. The glass transition (Tg), crystallization and melting temperatures (Tc and Tm) are listed in Table 10.

Table 10. Thermal transitions relative to all polymers.

DSC	PBF	PCH3DF	PFDMF
Tg (ºC)	15	–	–
Tc (ºC)	65	215	–
Tm (ºC)	135	255	–

The DSC analysis of precipitated PBF indicated a high degree of crystallinity, i.e. no glass transition detected and a melting endotherm at 130-140 ºC during the heating of the precipitated polymer from -40 to 200 ºC (1st DSC trace).[78] After quenching it from the melt in liquid nitrogen, the ensuing amorphous domains of PBF displayed a glass transition at ~15 ºC (~30 ºC lower than that of PBT)[79] and a well-defined crystallization exotherm with a maximum at ~65 ºC (~120 ºC lower than that of PBT),[78] which confirms its high aptitude to crystallize (Fig. 48). This was followed by a well-defined melting endotherm at ~135 ºC (~80 ºC lower than that of PBT).[78,79] When compared with its PEF and PPF homologues, PBF has the lowest thermal transition temperatures, which is in accordance with the higher macromolecular flexibility given by the additional methylene moiety in each polymer unit.[20,21,66,67] The significant

differences between PBF and its petrobased counterpart PBT, may constitute a downside for it to become a potential alternative for the latter.

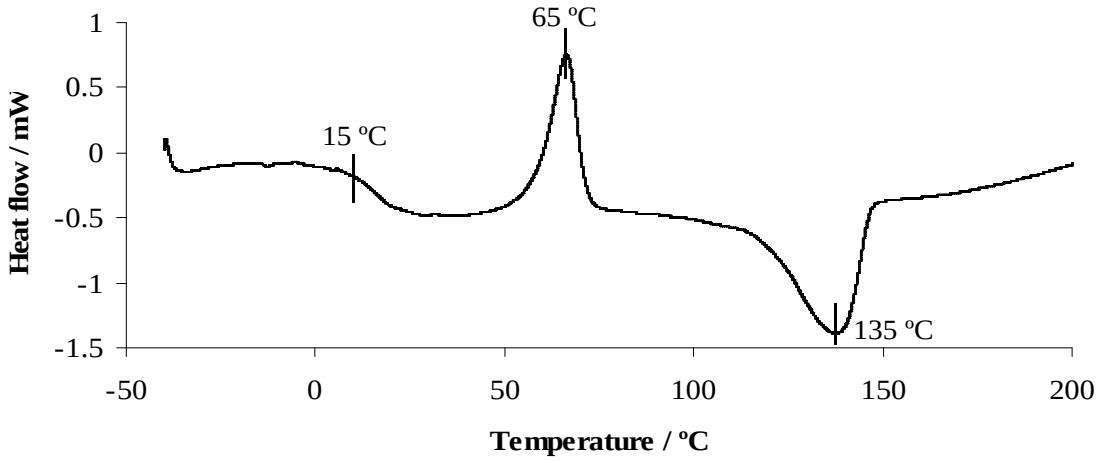


Fig. 48. DSC thermogram of PBF after quenching it from the melt in liquid nitrogen.

As for PBF, the 1st DSC trace of precipitated PCHDF did not show any glass transition features and presented a melting endotherm at ~255 ºC, which suggests a high degree of crystallinity. This Tm value is ~30 ºC lower than that of its petrobased counterpart, PCT (prepared with the normal 30/70 *cis*/*trans* isomer ratio).[73] After quenching from the melt in liquid nitrogen (Fig. 49), the ensuing amorphous domains of PCHBF did not present a defined glass transition and only a low intensity exothermic peak, corresponding to its crystallization, was observed at ~215 ºC. Its high aptitude to crystallize is corroborated by the same melting pattern as that of the 1st DSC trace. Its rather rapid crystallization and high Tm are very similar with those for PCT, which may make this material a very promising alternative for the latter.[73]

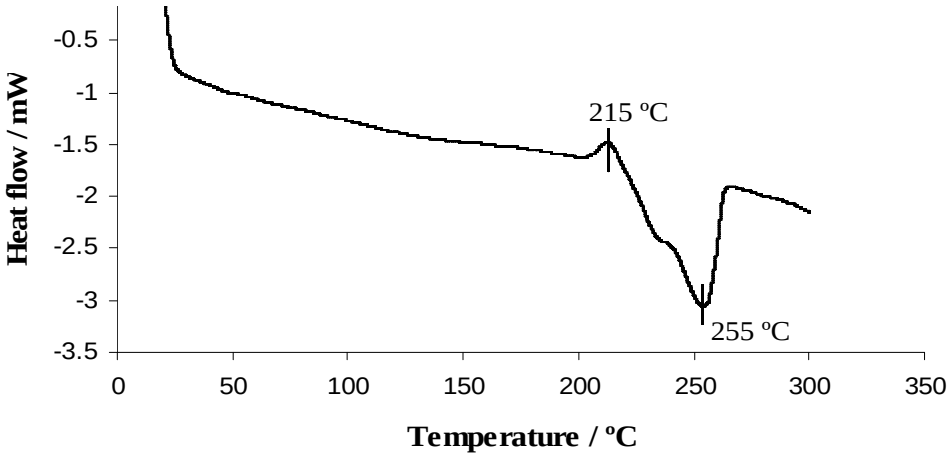


Fig. 49. DSC thermogram of PCHDF after quenching it from the melt in liquid nitrogen.

The fully furanic polyester, PFDMF, did not display any thermal transition during the successive DSC traces before and after quenching from 170 ºC, i.e. ~its Ti.

5.2.2.4. X-ray diffraction

The X-ray diffraction analysis of all polyesters aimed at assessing or confirming their degree of crystallinity, by taking into account the conclusions drawn from DSC.

The pronounced crystallinity of PBF was confirmed by the presence of three sharp peaks in its X-ray diffractogram (Fig. 50), respectively, at 2θ = 17.9, 22.7, and 25.2º. This pattern is similar to that displayed by its PPF homologue.[21,67]

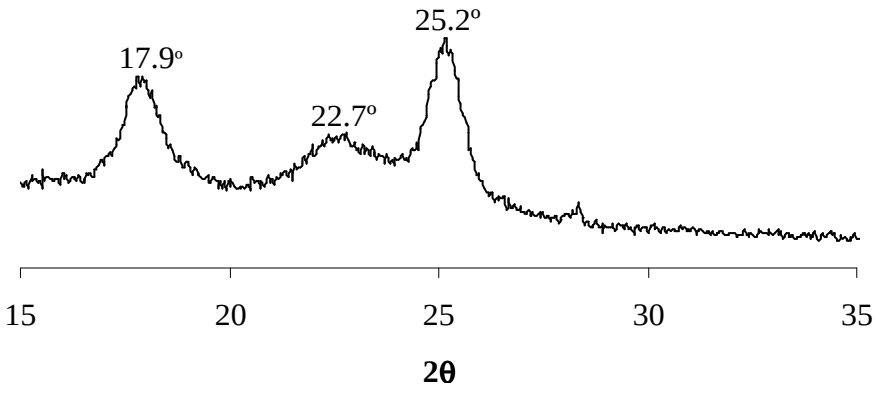


Fig. 50. Typical X-ray diffractogram of PBF.

The X-ray diffractogram of PCHDF (Fig. 51) gave two peaks characteristic of the crystalline morphology of the polymer at 2θ = 16.7 and 22.2º. This pattern is similar to that displayed by similar structures bearing *cis*/*trans*-1,4-cyclohexylenedimethylene moieties.[80] The poor definition of the peaks may be associated with the opposite conformational asymmetry conferred by the *cis*-cyclohexylenedimethylene moieties.

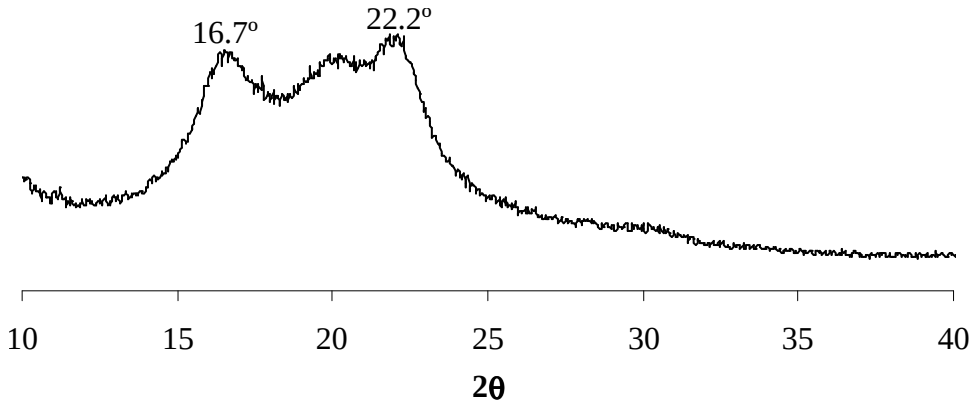


Fig. 51. Typical X-ray diffractogram of PCHBF.

The X-ray diffraction pattern of PFDMF (Fig. 52) gave peaks at 2θ = 14.9, 19.1, 21.9, 24.6, and 29.9º, which may suggest a high degree of macromolecular order.

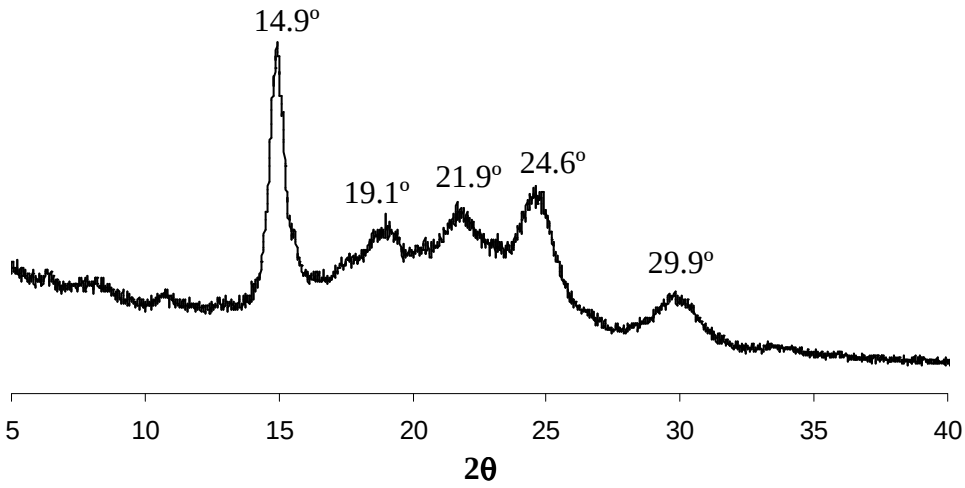


Fig. 52. Typical X-ray diffractogram of PFDMF.

6. Conclusions

It has been shown that the use of conventional polycondensation techniques represents a reliable way for the synthesis of novel polymeric materials, based on 2,5-furandicarboxylic acid derivatives and several diols, possessing regular structures and reasonably high molecular weights, as suggested by FTIR and ^{1}H and ^{13}C NMR spectroscopy.

As expected, the melt polycondensation has showed to be a successful way of preparing polyesters when volatile diols are used, whereas interfacial polycondensation has showed to be a reliable alternative when non-volatile aromatic diols are used.

All polymers were found to have a semi-crystalline morphology, as suggested by DSC and/or X-ray diffraction, and their thermal properties varied significantly with the nature of the diol. While furan-aliphatic polymers, PBF and PCHDF, have showed to be thermally stable up to ~300 ºC, the fully furan polymer was found to start degrading at ~180 ºC, as indicated by TGA. Furthermore, no Tg and melting features were detected for the latter during the successive DSC traces from -40 to 170 ºC. PBF was found to have a thermal behaviour identical to its PTF and PEF homologs, with Tg at ~15, Tc at ~65, and Tm at ~135 ºC, respectively. PCHDF did not display any Tg and its crystalline morphologies started melting at ~255 ºC.

Concluding, while furan-aliphatic polyesters, PBF and PCHDF, present promising properties for applications such as injection molding, fibers production, etc., the fully furanic polyester, given its poor thermal stability, may be used for applications that do not require temperatures above ~170 ºC.

7. Experimental

7.1. Materials

The commercial diols, CHDM (99%, mixture of cis and trans), and BDO (99%), were purchased from Sigma-Aldrich and were used without further purification, since their purity, as confirmed by ^{1}H and ^{13}C NMR spectroscopy (see section 7.1.1), was found to be adequate for their use. FDCA, as mentioned earlier, was generously offered and used as starting material for the synthesis of DMFDC and FDCDCl. All catalysts used for monomers and polymers synthesis were commercially available. All solvents used for synthesis, purification and characterization purposes were high-purity grade and used as received, except TCE, which was dried by adding sodium hydride.

7.1.1. ^{1}H and ^{13}C NMR data relative to all diols

All diols were characterized by ^{1}H and ^{13}C NMR spectroscopy in order to confirm their structure and purity. The data collected from ^{1}H and ^{13}C NMR spectroscopy of BDO and BHMF are listed in Table 11 and Table 12 respectively.

Table 11. Assignment of the ^{1}H NMR chemical shifts relative to BDO and BHMF; multiplicity (m); number of protons (nH).

^{1}H NMR	**BDO** (CD_3OD)	**BHMF** (C_3D_6O)
	δ (ppm); m; nH	
H-3,4	–	6.2; s; 2H
$C\underline{H}_2OH$	3.7; t; 4H	4.5; s; 4H
$C\underline{H}_2CH_2OH$	1.7; t; 4H	–
OH	3.0; s; 2H	4.2; s; 2H

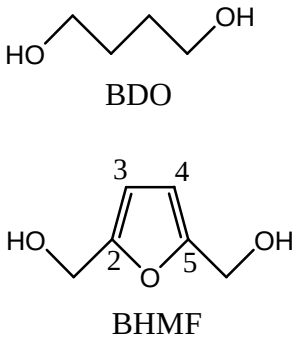


Table 12. Assignment of the ^{13}C NMR chemical shifts relative to BDO and BHMF.

^{13}C NMR	**BDO** (CD_3OD)	**BHMF** (C_3D_6O)
C-2,5	–	155.8
C-3,4	–	108.2
CH_2OH	62.6	57.2
$\underline{C}H_2CH_2OH$	29.8	–

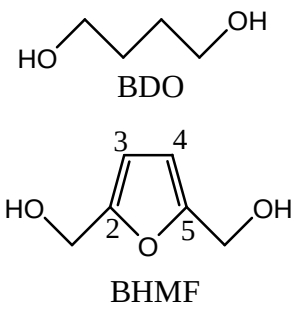


Fig. 53 shows the ^{1}H NMR spectrum of CHDM. All the attributions were made by comparing with the data reported for *trans*-cyclohexanedimethanol and *cis/trans*-cyclohexanedimethanol reported in the literature.[76] As it can be seen from the values of integration, the *cis*-isomer comprises about 30% of its composition, whereas the *trans*-isomer comprises about 70%.

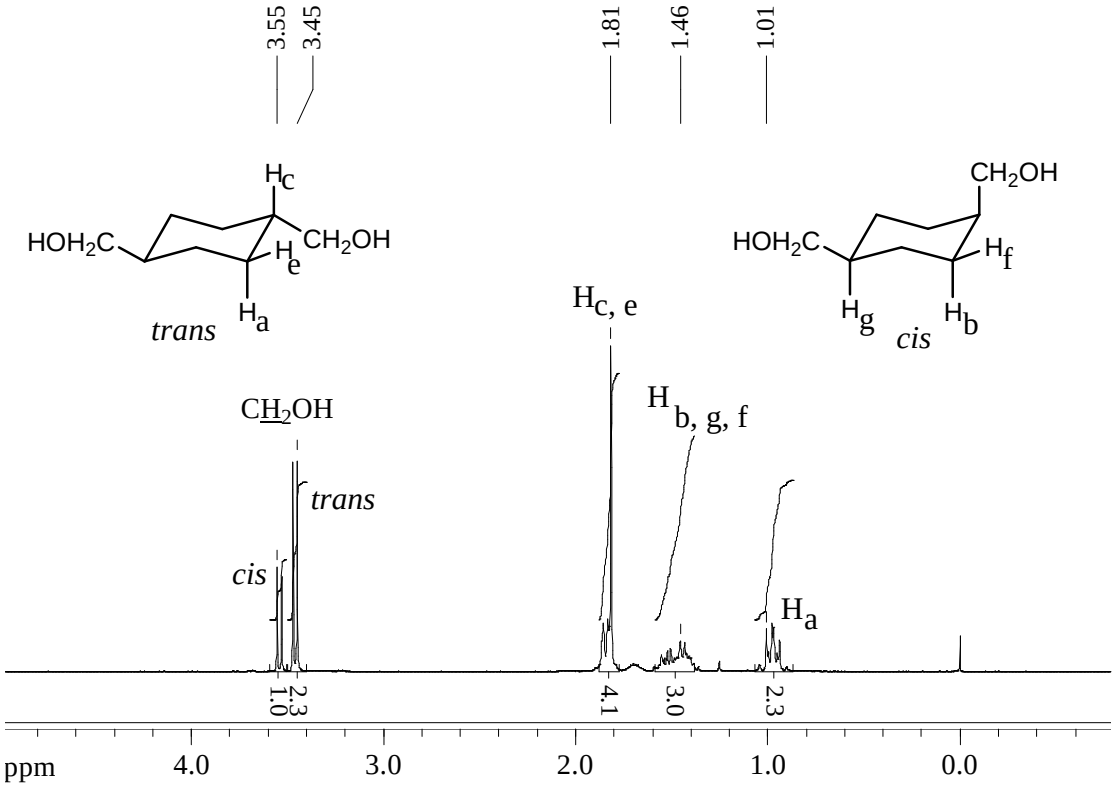


Fig. 53. Typical ^{1}H NMR spectrum of CHDM recorded in CD_3OD (ppm from TMS).

7.2. Analytical techniques

7.2.1. Fourier transform infrared spectroscopy

All FTIR spectra were obtained in a Mattson 7000 galaxy series spectrophotometer equipped with an ATR Golden Gate accessory, which allows the measure of attenuated total reflectance (FTIR-ATR). The spectra were acquired in the range 4000-400 cm^{-1} with a resolution of 8 cm^{-1} and 256 *scans*.

7.2.2. Nuclear magnetic resonance

^{1}H and ^{13}C NMR spectra were recorded on a Brücker AMX 300 spectrophotometer operating at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C. The chemical shifts were registered in parts per million (ppm) using tetramethylsilane

(TMS) as internal standard. Various deuterated solvents were used, viz. HFP (C_3F_6DOD), chloroform ($CDCl_3$), acetone (C_3D_6O), TCE ($C_2D_2Cl_4$), and methanol (CD_3OD).

7.2.3. Differential scanning calorimetry

DSC thermograms were obtained in a Setaram DSC92 calorimeter using aluminium crucibles, under nitrogen atmosphere, with a flow of 20 mL/min, and in the range of temperatures of 18 to 400 ºC. The scan rate was 10 ºC/min. Samples were prepared by adding 4-8 mg of compound to the crucible.

7.2.4. Thermogravimetry

TGA thermograms were obtained in a Shimadzu TGA 50 analyser using platinum crucibles, under nitrogen atmosphere, with a flow of 20 mL/min, and temperature increasing from 15 to 800 ºC. The constant heating rate was 10 ºC/min. Samples were prepared by adding 7-10 mg of compound to the crucible.

7.2.5. Elemental analysis

The results of elemental analysis (C, H) were obtained by using a Carlo Erba Elemental analyser in Spain at Centro de Apoio Científico e Tecnolóxico á Investigación Centre (CACTI) de la Universidade de Vigo.

7.2.6. X-ray diffraction

X-ray diffractograms were recorded with a Philips X'pert MPD diffractometer, using CuKα radiation.

7.3. Monomer synthesis

7.3.1. 2,5-Furandicarbonyl dichloride

Essentially according to the method of Gandini *et al*.,[21,66] 40 ml of $SOCl_2$ and 400 µl of DMF were added to a round-bottom flask of 100 ml containing FDCA, 20 g (0.128 mol). The reaction mixture was then heated to 80 ºC with stirring for 4 h under reflux, and both HCl and SO_2 released were trapped in NaOH aqueous solution. Upon 4 h, and after cooling the reaction mixture to room temperature, the excesses of $SOCl_2$ and DMF were removed under vacuum at room temperature, and collected in a trap cooled at liquid N_2 temperature. The product was purified by successive vacuum sublimations

to give white crystals in 70% yield, which recrystallized in n-hexane as white needles; m.p. 79 ºC (lit.[56] 80 ºC); FTIR (ν/cm^{-1}) 3140 and 3110 (furan =CH), 1737 (C=O), 1563 (furan C=C) and the typical peaks of ring breathing (1007) and of 2,5-disubstituted furans (974, 824 and 712); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, δ/ppm) 7.5 (2H, s, furan H-3,4); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, δ/ppm) 155.9 (C=O), 149.3 (furan C-2,5) and 123.2 (furan C-3,4).

7.3.2. Dimethyl 2,5-furandicarboxylate

In analogy to a procedure reported by Gandini *et al*.,[21,66] 7,5 ml of concentrated HCl and an excess of methanol (180 ml) were added to a 250 ml round-bottom flask containing FDCA, 15 g (0.096 mol). The reaction mixture was then heated to 80 ºC with stirring, for 6 h under reflux. Then, the reaction mixture was cooled to room temperature, leading to the crystallization of the main bulk of the ester, which was then isolated and collected by filtration; the remainder, which stayed in the mother liquor, was isolated by evaporating the mother liquor on the rotary evaporator. The purification of the monomer was carried out by precipitating the impurities in acetone by consecutively mixing the solids with it and filtrating. The soluble fraction containing the diester was then brought to the rotary evaporator in order to evaporate the solvent, resulting in a white solid in 50% yield; m.p. ~110 ºC (lit.[55,69] 110-111 ºC); FTIR (ν/cm^{-1}) 3171 and 3142 (furan =CH), 2975 (methyl CH_3), 1712 (C=O), 1581 and 1528 (furan C=C), 1292 (ester C-O) and the typical peaks of ring breathing (1027) and of 2,5-disubstituted furans (976, 828 and 757); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, δ/ppm) 7.2 (2H, s, furan H-3,4) and 3.9 (6H, s, 2,5-$COOCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, δ/ppm) 158.4 (C=O), 146.6 (furan C-2,5), 118.4 (furan C-3,4) and 52.4 (2,5-$COO\underline{C}H_3$).

7.4. Polymer synthesis

7.4.1. Poly(2,5-furandimethylene 2,5-furandicarboxylate)

Following the procedure of Gandini *et al*.,[21,66] two pre-prepared solutions were added, successively and quickly, to a flask equipped with a mechanical stirrer, condenser and thermometer, a first one (aqueous solution) containing 0.7 g of NaOH, 0.571 g (5.18 mmol) of BHMF (diol), and 72.4 mg of TBAB in 90 ml of distilled water, and a second one containing 0.996 g (5.18 mmol) of the diacid dichloride in 50 ml of DCM under mechanical agitation (900 r.p.m); it is important to take into account that the phase-transfer agent, the TBAB, must be added to the basic aqueous solution

containing the diol, just before mixing it with the organic solution containing the diacid chloride. The reaction instantaneously began (confirmed by the increase in viscosity) and proceeded for more 2 h at 24 ºC. Then, after stopping stir, concentrated H_2SO_4 was added to the solution to fall the pH down to 2. The ensuing polyester was then isolated by filtration with methanol (oligomers which are soluble in methanol passed through the filter paper) and then sequentially washed with the same solvent, just before placed in the oven at 40 ºC for 12 h. After dissolving in HFP, precipitating in an excess of methanol, isolating by filtration and drying, the polyester showed itself as brown crystals, 60% yield. FTIR (ν/cm^{-1}) 3129 (furan =CH), 2964 and 2880 (methylene CH_2), 1716 (C=O), 1580 and 1525 (furan C=C), 1267 (ester C-O) and the typical peaks of ring breathing (1003) and of 2,5-disubstituted furans (957, 837 and 764); ^{1}H NMR (300 MHz, C_3F_6DOD, TMS, δ/ppm) 7.3 (2H, s, furan H-3,4), 6.5 (2H, s, furan H-3',4') and 5.3 (4H, s, $COOCH_2$); ^{13}C NMR (75 MHz, C_3F_6DOD, TMS, δ/ppm) 160.6 (C=O), 149.9 (C-2,5), 147.1 (C-2',5'), 120.6 (C-3,4), 113.4 (C-3',4'), and 60.2 (2,5-COO$\underline{C}H_2$).

7.4.2. Poly(1,4-cyclohexylenedimethylene 2,5-furandicarboxylate)

In analogy to a procedure reported by Kharas *et al.*[74] 0.59 g of CHDM (4.13 mmol, in 1.5 excess) was placed in a polymerization tube. DMFDC, 0.5 g (2.75 mmol), and calcium acetate, 2.4 mg (0.013 mmol) were added and the system was heated in a silicon bath till 110 ºC, under a nitrogen atmosphere. The temperature of the system was raised to 180 ºC over the course of 2.5 h. The system was evacuated to ~10^{-3} bar and the temperature was progressively raised to 220 ºC in steps of 10 ºC. Upon cooling, a hard, dark brown solid was obtained. The product was then dissolved in HFP, precipitated in an excess of methanol, and isolated by filtration, resulting in a light brown solid, ~65% yield. FTIR (ν/cm^{-1}) 3149 and 3113 (furan =CH), 2923 and 2855 (methine CH and methylene CH_2), 1718 (C=O), 1577 and 1509 (furan C=C), 1270 (ester C-O) and the typical peaks of ring breathing (1018) and of 2,5-disubstituted furans (976, 827 and 764); ^{1}H NMR (300 MHz, C_3F_6DOD, TMS, δ/ppm) 7.3 (2H, s, furan H-3,4), 4.2 (4H, s, 2,5-$COOCH_2$ in the *cis*-isomer), 4.1 (4H, s, 2,5-$COOCH_2$ in the *trans*-isomer), 1.9-1.6 (6H, m, eq H-6,7 in the *trans*-isomer), 1.5-1.4 (10H, m, H-6,7 in the *cis*-isomer), 1.0 (4H, m, ax H-7 in the *trans*-isomer); ^{13}C NMR (75 MHz, C_3F_6DOD, TMS, δ/ppm) 161.4 (C=O), 146.9 (C-2,5), 119.8 (C-3,4), 72.3 (2,5-COO$\underline{C}H_2$ in the *trans*-isomer), 70.3 (2,5-COO$\underline{C}H_2$ in the *cis*-isomer), 24.7 and 28.2 (C-7 in the *cis*- and *trans*-isomers, respectively), and 35.1 and 37.6 (C-6 in the *cis*- and *trans*-isomers, respectively).

7.4.3. Poly(butylene 2,5-furandicarboxylate)

The procedure adopted for PCHDF was generally followed, except that the temperature of evacuation of the system to 10^{-3} bar was 160 ºC (different from the 180 ºC for PCHDF). The resulting polymer, after purification by precipitation of the HFP solution in an excess of methanol and subsequent filtration and drying, showed itself as a light brown solid, ~55% yield. FTIR (ν/cm^{-1}) 3154 and 3120 (furan =CH), 2965 and 2897 (methylene CH_2), 1716 (C=O), 1576 and 1525 (furan C=C), 1271 (ester C-O) and the typical peaks of ring breathing (1032) and of 2,5-disubstituted furans (967, 862 and 766); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, δ/ppm) 7.2 (2H, s, furan H-3,4), 4.4 (4H, s, 2,5-$COOCH_2$), 3.9 (4H, s, CH_2OCH_2) and 1.9 (4H, s, 2,5-$COOCH_2C\underline{H}_2$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, δ/ppm) 157.9 (C=O), 146.7 (C-2,5), 118.5 (C-3,4), 64.9 (2,5-$COO\underline{C}H_2$), 52.4 (CH_2OCH_2), and 25.2 (2,5-$COOCH_2\underline{C}H_2$).

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